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Supporting Information

Asymmetric Imino-Acylation of Alkenes Enabled by HAT-Photo/Nickel Cocatalysis

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General information

¹H, ¹³C, and ¹⁹F spectra were recorded in CDCl₃ solution on Bruker Aescend 400 MHz and 500 MHz instruments. ¹⁹F NMR were reported as ¹⁹F exp. comp. pulse decoupling (¹⁹F CPD). The chemical shifts are given in ppm relative to the resonance of the solvent [1 H: δ (CDCl₃) = 7.26, 13 C: δ (CDCl₃) = 77.16 ppm] or relative to tetramethylsilane [1 H: δ (SiMe₄) = 0.00 ppm] as an internal standard. Multiplicities are given as: s (singlet); d (doublet); t (triplet); q (quartet); dd (doublet of doublets); m (multiplets), etc. Coupling constants are reported as J values in Hz. High resolution mass spectral analysis (HRMS) was performed on Waters XEVO G2 Q-TOF. HPLC analysis was performed on Thermo UltiMate 3000. Enantiomer excesses were determined by HPLC analysis employing Daicel chiral column (chiralpak IA, chiralpak AD-H) or Guangzhou FLM Scientific Instrument chiral column (chiral MD) with n-hexane/i-PrOH as the eluents. Flash chromatography was performed using 300-400 mesh silica gel with the indicated solvent system. All air- or moisture-sensitive reactions were protected with nitrogen atmosphere. All reactions were monitored through thin layer chromatography [Merck 60 F254 precoated silica gel plate (0.2 mm thickness)]. Subsequent to elution, spots were visualized using UV radiation (254 nm) on Spectroline Model ZF-7 254 nm. Other visualization methods include staining with a basic solution of potassium permanganate or acidic solution of ceric ammonium molybdate, followed by heating.

Unless otherwise noted, all reagents and starting materials were purchased from commercial vendors and used as received without further purification. TBADT (tetrabutyl ammonium decatungstate) were synthesized according to the reported method^[1].

Synthesis of Starting Materials

All the aldehydes 1a–1y used are commercially available. The oxime esters 2a^[2], 2a-1^[3], 2a-2^[4], 2b^[2], 2d^[2], 2f–2h^[2], 2l^[2], and 2u^[2] are known compounds in the literature, and their NMR data are consistent to the reported ones. The oxime esters 2c, 2e, 2i–2k, 2m–2t, and 2v were prepared according to the procedure reported in the literature. ^[2]

General procedure:

(1-Allylcyclohexyl)(phenyl)methanone *O*-(2,4,6-trimethylbenzoyl) oxime (2c)

The title compound was isolated as a colorless oil (0.51 g, 1.3 mmol, 13% yield over three steps on 10 mmol scale).

¹**H NMR** (500 MHz, Chloroform-*d*) δ = 7.38 – 7.30 (m, 3H), 7.14 (d, *J* = 7.9 Hz, 2H), 6.73 (s, 2H), 6.04 – 5.94 (m, 1H), 5.21 – 5.12 (m, 2H), 2.38 (d, *J* = 7.2 Hz, 2H), 2.21 (s, 3H), 2.09 (s, 6H), 1.98 – 1.89 (m, 2H), 1.71 – 1.62 (m, 2H), 1.61 – 1.42 (m, 6H). ppm.

¹³C NMR (126 MHz, Chloroform-*d*) δ = 173.1, 167.7, 139.3, 135.8 (2C), 133.9, 133.1, 129.4, 128.34, 128.26 (2C), 128.0 (2C), 126.9 (2C), 118.0, 45.2, 41.1, 33.6 (2C), 26.0, 22.2 (2C), 21.1, 19.8 (2C) ppm.

HRMS (ESI) m/z calculated for $C_{26}H_{31}NO_2H^+$ [M+H]⁺: 390.2428, found: 390.2428.

2-Methyl-1-phenylpent-4-en-1-one *O*-(2,4,6-trimethylbenzoyl) oxime (2e)

The title compound was isolated as a yellow oil (0.47 g, 1.4 mmol, 28% yield over three

steps on 5 mmol scale).

¹H NMR (500 MHz, Chloroform-*d*) δ = 7.53 (d, J = 6.3 Hz, 2H), 7.45 – 7.37 (m, 3H), 6.90 (s, 2H), 5.74 – 5.64 (m, 1H), 5.03 – 4.95 (m, 2H), 3.54 – 3.45 (m, 1H), 2.44 – 2.39 (m, 1H), 2.38 (s, 6H), 2.32 (s, 3H), 2.22 – 2.16 (m, 1H), 1.25 (d, J = 7.1 Hz, 3H) ppm. ¹³C NMR (126 MHz, Chloroform-*d*) δ = 171.7, 167.6, 139.9, 135.70 (2C), 135.66, 134.3, 129.8, 129.7, 128.5 (2C), 128.4 (4C), 117.2, 38.1, 35.6, 21.4, 19.9 (2C), 17.7 ppm.

HRMS (ESI) m/z calculated for C₂₂H₂₅NO₂Na⁺ [M+Na]⁺: 358.1778, found: 358.1777.

2,2-Dimethyl-1-(4-(trifluoromethoxy)phenyl)pent-4-en-1-one *O*-(2,4,6-trimethylbenzoyl) oxime (2i)

The title compound was isolated as a yellow oil (1.43 g, 3.3 mmol, 33% yield over three steps on 10 mmol scale).

¹**H NMR** (400 MHz, Chloroform-*d*) δ = 7.23 (d, J = 8.3 Hz, 2H), 7.15 (d, J = 8.8 Hz, 2H), 6.75 (s, 2H), 6.02 – 5.86 (m, 1H), 5.22 – 5.07 (m, 2H), 2.37 (d, J = 6.9 Hz, 2H), 2.22 (s, 3H), 2.07 (s, 6H), 1.26 (s, 6H) ppm.

¹³C **NMR** (101 MHz, Chloroform-*d*) $\delta = 173.7$, 167.3, 149.2 (q, J = 1.8 Hz), 139.7, 135.9 (2C), 134.1, 132.0, 129.0, 128.7 (2C), 128.4 (2C), 120.6 (2C), 120.5 (q, J = 257.7 Hz), 118.5, 44.2, 41.7, 25.7 (2C), 21.1, 19.8 (2C) ppm.

¹⁹**F NMR** (376 MHz, Chloroform-*d*) δ = –57.81 (s, 3F) ppm.

HRMS (ESI) m/z calculated for $C_{24}H_{26}F_3NO_3Na^+$ [M+Na]⁺: 456.1757, found: 456.1757.

1-(4-Fluorophenyl)-2,2-dimethylpent-4-en-1-one *O*-(2,4,6-trimethylben-zoyl) oxime (2j)

The title compound was isolated as a white solid (1.47 g, 4.0 mmol, 40% yield over three steps on 10 mmol scale).

¹**H NMR** (500 MHz, Chloroform-*d*) δ = 7.10 – 7.03 (m, 4H), 6.74 (s, 2H), 5.99 – 5.89 (m, 1H), 5.18 – 5.09 (m, 2H), 2.36 (d, J = 7.3 Hz, 2H), 2.20 (s, 3H), 2.11 (s, 6H), 1.25 (s, 6H) ppm.

¹³C **NMR** (126 MHz, Chloroform-*d*) δ = 173.7, 167.3, 162.5 (d, J = 248.1 Hz), 139.5, 135.8 (2C), 134.1, 129.1 (d, J = 3.7 Hz), 129.0, 128.8 (d, J = 8.0 Hz, 2C), 128.3 (2C), 118.3, 115.2 (d, J = 21.7 Hz, 2C), 44.2, 41.6, 25.7 (2C), 21.0, 19.8 (2C) ppm.

¹⁹**F NMR** (471 MHz, Chloroform-*d*) δ = –112.67 (s, 1F) ppm.

HRMS (ESI) m/z calculated for $C_{23}H_{26}FNO_2Na^+$ [M+Na]⁺: 390.1841, found: 390.1840.

1-(4-Chlorophenyl)-2,2-dimethylpent-4-en-1-one *O*-(2,4,6-trimethylbenzoyl) oxime (2k)

The title compound was isolated as a yellow oil (1.49 g, 3.9 mmol, 39% yield over three steps on 10 mmol scale).

¹**H NMR** (400 MHz, Chloroform-*d*) δ = 7.34 (d, J = 8.4 Hz, 2H), 7.03 (d, J = 8.4 Hz, 2H), 6.75 (s, 2H), 6.00 – 5.86 (m, 1H), 5.20 – 5.07 (m, 2H), 2.35 (d, J = 7.2 Hz, 2H), 2.21 (s, 3H), 2.11 (s, 6H), 1.25 (s, 6H) ppm.

¹³C NMR (101 MHz, Chloroform-*d*) δ = 173.5, 167.3, 139.6, 135.9 (2C), 134.5, 134.1, 131.6, 129.0, 128.39 (2C), 128.36 (2C), 128.33 (2C), 118.5, 44.2, 41.6, 25.7 (2C), 21.1,

19.9 (2C) ppm.

HRMS (ESI) m/z calculated for $C_{23}H_{26}CINO_2Na^+$ [M+Na]⁺: 406.1544, found: 406.1550.

tert-Butyl 4-(2,2-dimethyl-1-(((2,4,6-trimethylbenzoyl)oxy)imino)pent-4-en-1-yl)-benzoate (2m)

The title compound was isolated as a white solid (0.99 g, 2.2 mmol, 22% yield over three steps on 10 mmol scale).

¹**H NMR** (500 MHz, Chloroform-*d*) δ = 7.97 (d, J = 8.2 Hz, 2H), 7.14 (d, J = 8.3 Hz, 2H), 6.66 (s, 2H), 5.95 – 5.86 (m, 1H), 5.15 – 5.04 (m, 2H), 2.33 (d, J = 7.3 Hz, 2H), 2.12 (s, 3H), 2.08 (s, 6H), 1.55 (s, 9H), 1.21 (s, 6H) ppm.

¹³C NMR (126 MHz, Chloroform-*d*) δ = 173.4, 167.0, 164.8, 139.3, 137.3, 135.6 (2C), 133.8, 131.8, 128.9 (2C), 128.8, 128.2 (2C), 126.7 (2C), 118.3, 81.1, 44.1, 41.3, 28.0 (3C), 25.5 (2C), 20.9, 19.7 (2C) ppm.

HRMS (ESI) m/z calculated for $C_{28}H_{35}NO_4H^+$ [M+H]⁺: 450.2639, found: 450.2643.

2,2-Dimethyl-1-(*m*-tolyl)pent-4-en-1-one *O*-(2,4,6-trimethylbenzoyl) oxime (2n)

The title compound was isolated as a yellow oil (1.56 g, 4.3 mmol, 43% yield over three steps on 10 mmol scale).

¹**H NMR** (500 MHz, Chloroform-*d*) δ = 7.23 (t, J = 8.0 Hz, 1H), 7.13 (d, J = 7.8 Hz, 1H), 6.92 – 6.86 (m, 2H), 6.73 (s, 2H), 6.02 – 5.90 (m, 1H), 5.19 – 5.07 (m, 2H), 2.38 (d, J = 7.3 Hz, 2H), 2.34 (s, 3H), 2.21 (s, 3H), 2.10 (s, 6H), 1.26 (s, 6H) ppm.

¹³C NMR (126 MHz, Chloroform-*d*) δ = 175.0, 167.6, 139.4, 137.6, 135.9 (2C), 134.4, 133.3, 129.4, 129.0, 128.3 (2C), 127.9, 127.4, 124.0, 118.2, 44.3, 41.6, 25.8 (2C), 21.5,

21.1, 19.8 (2C) ppm.

HRMS (ESI) m/z calculated for $C_{24}H_{29}NO_2H^+$ [M+H]⁺: 364.2271, found: 364.2278.

1-(3-Methoxyphenyl)-2,2-dimethylpent-4-en-1-one *O*-(2,4,6-trimethylbenzoyl) oxime (20)

The title compound was isolated as a yellow solid (2.16 g, 5.7 mmol, 57% yield over three steps on 10 mmol scale).

¹**H NMR** (400 MHz, Chloroform-*d*) δ = 7.23 (t, J = 7.9 Hz, 1H), 6.81 (d, J = 8.3 Hz, 1H), 6.69 (s, 2H), 6.64 (d, J = 7.6 Hz, 1H), 6.60 (s, 1H), 5.99 – 5.86 (m, 1H), 5.16 – 5.05 (m, 2H), 3.71 (s, 3H), 2.37 (d, J = 7.2 Hz, 2H), 2.16 (s, 3H), 2.09 (s, 6H), 1.24 (s, 6H) ppm.

¹³C NMR (101 MHz, Chloroform-*d*) δ = 174.4, 167.5, 159.1, 139.4, 135.8 (2C), 134.4, 134.3, 129.2, 129.1, 128.2 (2C), 119.2, 118.2, 113.4, 112.9, 55.1, 44.3, 41.5, 25.8 (2C), 21.0, 19.8 (2C) ppm.

HRMS (ESI) m/z calculated for $C_{24}H_{29}NO_3Na^+$ [M+Na]⁺: 402.2040, found: 402.2046.

1-(3-Fluorophenyl)-2,2-dimethylpent-4-en-1-one *O*-(2,4,6-trimethylbenzoyl) oxime (2p)

The title compound was isolated as a yellow oil (1.25 g, 3.4 mmol, 34% yield over three steps on 10 mmol scale).

¹**H NMR** (400 MHz, Chloroform-*d*) δ = 7.37 – 7.29 (m, 1H), 7.03 (t, J = 8.6 Hz, 1H), 6.87 (d, J = 7.6 Hz, 1H), 6.83 (d, J = 8.7 Hz, 1H), 6.74 (s, 2H), 6.00 – 5.87 (m, 1H), 5.20 – 5.09 (m, 2H), 2.38 (d, J = 7.2 Hz, 2H), 2.21 (s, 3H), 2.12 (s, 6H), 1.26 (s, 6H) ppm.

¹³C NMR (101 MHz, Chloroform-d) $\delta = 173.2$ (d, J = 1.5 Hz), 167.4, 162.2 (d, J =

247.5 Hz), 139.6, 135.9 (2C), 135.2 (d, J = 7.6 Hz), 134.1, 129.8 (d, J = 8.2 Hz), 129.0, 128.4 (2C), 122.7 (d, J = 3.3 Hz), 118.5, 115.4 (d, J = 20.9 Hz), 114.3 (d, J = 22.8 Hz), 44.2, 41.6, 25.7 (2C), 21.1, 19.8 (2C) ppm.

¹⁹**F NMR** (376 MHz, Chloroform-*d*) δ = –112.26 (s, 1F) ppm.

HRMS (ESI) m/z calculated for $C_{23}H_{26}OFNO_2H^+[M+H]^+$: 368.2020, found: 368.2027.

1-(3-Chlorophenyl)-2,2-dimethylpent-4-en-1-one *O*-(2,4,6-trimethylbenzoyl) oxime (2q)

The title compound was isolated as a yellow solid (1.45 g, 2.5 mmol, 25% yield over three steps on 10 mmol scale).

¹**H NMR** (400 MHz, Chloroform-*d*) δ = 7.32 – 7.23 (m, 2H), 7.08 (s, 1H), 6.99 – 6.93 (m, 1H), 6.73 (s, 2H), 5.98 – 5.86 (m, 1H), 5.18 – 5.07 (m, 2H), 2.35 (d, *J* = 7.1 Hz, 2H), 2.19 (s, 3H), 2.10 (s, 6H), 1.24 (s, 6H) ppm.

¹³C **NMR** (101 MHz, Chloroform-*d*) δ = 173.1, 167.3, 139.6, 135.9 (2C), 135.0, 134.2, 134.0, 129.5, 129.0, 128.6, 128.4 (2C), 126.9, 125.1, 118.6, 44.2, 41.6, 25.7 (2C), 21.1, 19.8 (2C) ppm.

HRMS (ESI) m/z calculated for $C_{23}H_{26}CINO_2Na^+$ [M+Na]⁺: 406.1544, found: 406.1549.

1-(3-Bromophenyl)-2,2-dimethylpent-4-en-1-one *O*-(2,4,6-trimethylbenzoyl) oxime (2r)

The title compound was isolated as a white solid (2.26 g, 5.3 mmol, 53% yield over three steps on 10 mmol scale).

¹**H NMR** (400 MHz, Chloroform-*d*) δ = 7.44 (d, J = 8.5 Hz, 1H), 7.25 – 7.18 (m, 2H), 7.01 (d, J = 7.7 Hz, 1H), 6.73 (s, 2H), 5.98 – 5.84 (m, 1H), 5.18 – 5.06 (m, 2H), 2.35

(d, J = 7.2 Hz, 2H), 2.20 (s, 3H), 2.11 (s, 6H), 1.24 (s, 6H) ppm.

¹³C NMR (101 MHz, Chloroform-*d*) δ = 173.0, 167.3, 139.6, 135.9 (2C), 135.2, 134.0, 131.5, 129.7 (2C), 129.0, 128.4 (2C), 125.6, 122.2, 118.6, 44.2, 41.6, 25.7 (2C), 21.1, 19.9 (2C) ppm.

HRMS (ESI) m/z calculated for $C_{23}H_{26}BrNO_2Na^+$ [M+Na]⁺: 450.1039, found: 450.1041.

2,2-Dimethyl-1-(3-(trifluoromethyl)phenyl)pent-4-en-1-one *O*-(2,4,6-trimethylbenzoyl) oxime (2s)

The title compound was isolated as a yellow solid (1.71 g, 4.1 mmol, 41% yield over three steps on 10 mmol scale).

¹**H NMR** (500 MHz, Chloroform-*d*) δ = 7.60 (d, J = 7.9 Hz, 1H), 7.49 (t, J = 7.8 Hz, 1H), 7.37 (s, 1H), 7.28 (d, J = 7.8 Hz, 1H), 6.74 (s, 2H), 5.99 – 5.89 (m, 1H), 5.20 – 5.09 (m, 2H), 2.37 (d, J = 7.2 Hz, 2H), 2.21 (s, 3H), 2.08 (s, 6H), 1.27 (s, 6H) ppm.

¹³C NMR (126 MHz, Chloroform-*d*) δ = 173.0, 167.3, 139.8, 136.0 (2C), 134.1, 134.0, 130.6 (q, J = 33.0 Hz), 130.5, 128.9, 128.8, 128.4 (2C), 125.3 (q, J = 3.7 Hz), 123.8 (q, J = 272.5 Hz), 123.8 (q, J = 3.8 Hz), 118.7, 44.3, 41.7, 25.7 (2C), 21.2, 19.8 (2C) ppm.

¹⁹**F NMR** (471 MHz, Chloroform-*d*) δ = -62.73 (s, 3F) ppm.

HRMS (ESI) m/z calculated for $C_{24}H_{26}F_3NO_2H^+$ [M+H]⁺: 418.1988, found: 418.1989.

1-(2-Fluorophenyl)-2,2-dimethylpent-4-en-1-one *O*-(2,4,6-trimethylbenzoyl) oxime (2t)

The title compound was isolated as a yellow oil (0.99 g, 2.7 mmol, 27% yield over three steps on 10 mmol scale).

¹**H NMR** (400 MHz, Chloroform-*d*) $\delta = 7.36 - 7.27$ (m, 1H), 7.14 (t, J = 7.4 Hz, 1H),

7.11 - 7.01 (m, 2H), 6.73 (s, 2H), 6.02 - 5.88 (m, 1H), 5.19 - 5.07 (m, 2H), 2.43 (d, J = 7.2 Hz, 2H), 2.20 (s, 3H), 2.13 (s, 6H), 1.29 (s, 3H), 1.23 (s, 3H) ppm.

¹³C NMR (101 MHz, Chloroform-*d*) δ = 169.2 (d, *J* = 1.7 Hz), 167.3, 158.0 (d, *J* = 246.9 Hz), 139.5, 135.9 (2C), 134.2, 130.5 (d, *J* = 7.9 Hz), 129.1, 128.3 (2C), 128.2, 123.7 (d, *J* = 3.4 Hz), 121.1 (d, *J* = 18.7 Hz), 118.3, 115.7 (d, *J* = 21.5 Hz), 44.2, 41.8, 25.5, 25.1, 21.1, 19.7 (2C) ppm.

¹⁹**F NMR** (376 MHz, Chloroform-*d*) δ = –111.75 (s, 1F) ppm.

HRMS (ESI) m/z calculated for C₂₃H₂₆FNO₂H⁺ [M+H]⁺: 368.2020, found: 368.2019.

2,2-Dimethyl-1-(thiophen-3-yl)pent-4-en-1-one O-(2,4,6-trimethylbenzoyl) oxime (2v)

The title compound was isolated as a white solid (2.26 g, 6.4 mmol, 64% yield over three steps on 10 mmol scale).

¹**H NMR** (400 MHz, Chloroform-*d*) δ = 7.32 – 7.28 (m, 1H), 7.13 – 7.08 (m, 1H), 6.90 (d, *J* = 5.0 Hz, 1H), 6.76 (s, 2H), 5.96 – 5.84 (m, 1H), 5.17 – 5.05 (m, 2H), 2.33 (d, *J* = 7.2 Hz, 2H), 2.23 (s, 3H), 2.12 (s, 6H), 1.27 (s, 6H) ppm.

¹³C NMR (101 MHz, Chloroform-*d*) δ = 171.3, 167.6, 139.6, 136.0 (2C), 134.3, 132.2, 129.2, 128.4 (2C), 127.4, 125.3, 122.9, 118.3, 44.4, 41.8, 25.7 (2C), 21.2, 19.8 (2C) ppm.

HRMS (ESI) m/z calculated for $C_{21}H_{25}NO_2SNa^+$ [M+Na]⁺: 378.1498, found: 378.1498.

General Procedure for Ni/Photo-Cocatalyzed Asymmetric Iminoacylation of Alkenes

Tetrabutyl ammonium decatungstate (TBADT) (33.2 mg, 0.01 mmol, 5 mol%), Ni(ClO₄)₂·6H₂O (11.0 mg, 0.03 mmol, 15 mol%), ligand **L1** (12.8 mg, 0.036 mmol, 18 mol%), NaClO₄ (12.2 mg, 0.1 mmol, 0.5 equiv), aldehydes **1** if solid (0.6 mmol, 3 equiv) and the oxime esters **2** (0.2 mmol, 1 equiv) were placed in an oven-dried test tube equipped with a magnetic stirring bar. The tube was evacuated and filled with nitrogen (three cycles). To these solids, anhydrous MeCN (1 mL, 0.2 M) and aldehydes **1** if liquid (0.6 mmol, 3 equiv) were added sequentially under nitrogen atmosphere. Subsequently, the reaction mixture was stirred and irradiated using two 34 W 390 nm LED lamps (Kessil PR160-390, 5 cm away, with adequate fans keep the reaction at room temperature) for 24 h. After exposing to air for 15 minutes, the reaction mixture was filtered through a pad of Celite and concentrated under reduced pressure. The residue was purified through column chromatography (silica gel, EtOAc/petroleum ether) to afford the desired products **3**.

(S)-1-(4,4-Dimethyl-5-phenyl-3,4-dihydro-2*H*-pyrrol-2-yl)pentan-2-one (3aa)

The title compound was isolated through column chromatography (silica gel, petroleum ether/ethyl acetate = 5:1) as a colorless oil (34.0 mg, 66% yield).

¹**H NMR** (500 MHz, Chloroform-*d*) δ = 7.66 (d, J = 8.0 Hz, 2H), 7.41 – 7.32 (m, 3H), 4.45 – 4.36 (m, 1H), 3.10 (dd, J = 16.4, 5.4 Hz, 1H), 2.54 (dd, J = 16.4, 8.6 Hz, 1H), 2.51 – 2.41 (m, 2H), 2.23 (dd, J = 12.6, 6.7 Hz, 1H), 1.69 – 1.58 (m, 2H), 1.49 (dd, J = 12.6, 8.8 Hz, 1H), 1.35 (s, 3H), 1.33 (s, 3H), 0.93 (t, J = 7.4 Hz, 3H) ppm.

¹³C NMR (126 MHz, Chloroform-*d*) δ = 210.1, 180.1, 134.7, 129.6, 128.3 (2C), 128.0 (2C), 64.1, 50.8, 49.8, 48.6, 45.6, 27.4, 25.9, 17.3, 13.9 ppm.

HRMS (ESI) m/z calculated for C₁₇H₂₃NOH⁺ [M+H]⁺: 258.1582, found: 258.1857.

HPLC-Data: 99% *ee*, (Chiral MD column, $\lambda = 254$ nm, hexane/isopropanol = 90/10, flow rate = 0.5 mL/min): $t_R = 10.1$ (minor), 10.8 (major).

(S)-1-(4,4-Dimethyl-5-phenyl-3,4-dihydro-2*H*-pyrrol-2-yl)heptan-2-one (3ba)

The title compound was isolated through column chromatography (silica gel, petroleum ether/ethyl acetate = 5:1) as a colorless oil (38.8 mg, 68% yield).

¹**H NMR** (500 MHz, Chloroform-*d*) δ = 7.67 (d, J = 8.1 Hz, 2H), 7.42 – 7.33 (m, 3H), 4.44 – 4.36 (m, 1H), 3.11 (dd, J = 16.3, 5.4 Hz, 1H), 2.55 (dd, J = 16.4, 8.7 Hz, 1H), 2.52 – 2.42 (m, 2H), 2.23 (dd, J = 12.5, 6.7 Hz, 1H), 1.66 – 1.57 (m, 2H), 1.50 (dd, J = 12.6, 8.8 Hz, 1H), 1.35 (s, 3H), 1.33 (s, 3H), 1.32 – 1.24 (m, 4H), 0.89 (t, J = 6.9 Hz, 3H) ppm.

¹³C NMR (126 MHz, Chloroform-*d*) δ = 210.2, 180.1, 134.8, 129.6, 128.3 (2C), 128.0 (2C), 64.2, 50.8, 49.8, 48.6, 43.7, 31.5, 27.4, 26.0, 23.6, 22.6, 14.1 ppm.

HRMS (ESI) m/z calculated for C₁₉H₂₇NOH⁺ [M+H]⁺: 286.2165, found: 286.2166.

HPLC-Data: 97% *ee*, (Chiral MD column, $\lambda = 254$ nm, hexane/isopropanol = 95/5, flow rate = 0.5 mL/min): $t_R = 12.9$ (minor), 14.3 (major).

(S)-1-(4,4-Dimethyl-5-phenyl-3,4-dihydro-2*H*-pyrrol-2-yl)-4-methylpentan-2-one (3ca)

The title compound was isolated through column chromatography (silica gel, petroleum ether/ethyl acetate = 5:1) as a colorless oil (33.6 mg, 62% yield).

¹**H NMR** (400 MHz, Chloroform-*d*) δ = 7.66 (d, J = 7.9 Hz, 2H), 7.42 – 7.32 (m, 3H), 4.46 – 4.34 (m, 1H), 3.12 (dd, J = 16.6, 5.2 Hz, 1H), 2.52 (dd, J = 16.5, 8.8 Hz, 1H),

2.42 - 2.32 (m, 2H), 2.24 (dd, J = 12.6, 6.7 Hz, 1H), 2.21 - 2.13 (m, 1H), 1.49 (dd, J = 12.6, 8.8 Hz, 1H), 1.35 (s, 3H), 1.33 (s, 3H), 0.93 (d, J = 6.6 Hz, 6H) ppm.

¹³C NMR (101 MHz, Chloroform-*d*) δ = 209.8, 180.1, 134.7, 129.6, 128.3 (2C), 128.0 (2C), 64.0, 52.7, 50.8, 50.3, 48.6, 27.4, 25.9, 24.7, 22.74, 22.70 ppm.

HRMS (ESI) m/z calculated for C₁₈H₂₅NOH⁺ [M+H]⁺: 272.2009, found: 272.2009.

HPLC-Data: 90% *ee*, (Chiral MD column, $\lambda = 254$ nm, hexane/isopropanol = 95/5, flow rate = 0.5 mL/min): $t_R = 12.0$ (minor), 13.8 (major).

(S)-1-(4,4-Dimethyl-5-phenyl-3,4-dihydro-2*H*-pyrrol-2-yl)-4,4-dimethylpentan-2-one (3da)

The title compound was isolated through column chromatography (silica gel, petroleum ether/ethyl acetate = 6:1) as a colorless oil (34.8 mg, 61% yield).

¹**H NMR** (400 MHz, Chloroform-*d*) δ = 7.66 (d, J = 7.9 Hz, 2H), 7.41 – 7.33 (m, 3H), 4.45 – 4.35 (m, 1H), 3.18 (dd, J = 16.8, 4.9 Hz, 1H), 2.53 (dd, J = 16.8, 9.1 Hz, 1H), 2.42 – 2.33 (m, 2H), 2.26 (dd, J = 12.6, 6.7 Hz, 1H), 1.49 (dd, J = 12.6, 8.8 Hz, 1H), 1.35 (s, 3H), 1.33 (s, 3H), 1.04 (s, 9H) ppm.

¹³C NMR (101 MHz, Chloroform-*d*) δ = 209.7, 180.2, 134.7, 129.7, 128.3 (2C), 128.0 (2C), 64.0, 55.7, 52.1, 50.8, 48.6, 31.3, 29.9 (3C), 27.4, 25.9 ppm.

HRMS (ESI) m/z calculated for C₁₉H₂₇NOH⁺ [M+H]⁺: 286.2165, found: 286.2168.

HPLC-Data: 94% *ee*, (Chiral MD column, $\lambda = 254$ nm, hexane/isopropanol = 95/5, flow rate = 0.5 mL/min): $t_R = 11.5$ (minor), 12.2 (major).

(S)-1-(4,4-Dimethyl-5-phenyl-3,4-dihydro-2*H*-pyrrol-2-yl)-4-phenylbutan-2-one (3ea)

The title compound was isolated through column chromatography (silica gel, petroleum ether/ethyl acetate = 5:1) as a colorless oil (36.4 mg, 57% yield).

¹**H NMR** (500 MHz, Chloroform-*d*) δ = 7.67 (d, J = 8.2 Hz, 2H), 7.41 – 7.34 (m, 3H), 7.30 – 7.26 (m, 2H), 7.23 – 7.18 (m, 3H), 4.45 – 4.37 (m, 1H), 3.09 (dd, J = 16.2, 5.7 Hz, 1H), 2.98 – 2.92 (m, 2H), 2.89 – 2.78 (m, 2H), 2.55 (dd, J = 16.2, 8.4 Hz, 1H), 2.20 (dd, J = 12.6, 6.8 Hz, 1H), 1.48 (dd, J = 12.6, 8.8 Hz, 1H), 1.35 (s, 3H), 1.32 (s, 3H) ppm.

¹³C NMR (126 MHz, Chloroform-*d*) δ = 209.0, 180.2, 141.2, 134.6, 129.7, 128.6 (2C), 128.5 (2C), 128.3 (2C), 128.0 (2C), 126.2, 64.1, 50.8, 50.0, 48.5, 45.2, 29.8, 27.4, 25.9 ppm.

HRMS (ESI) m/z calculated for $C_{22}H_{25}NOH^+$ [M+H]⁺: 320.2009, found: 320.2010. **HPLC-Data**: 95% *ee*, (Chiralpak IA column, $\lambda = 254$ nm, hexane/isopropanol = 90/10, flow rate = 0.5 mL/min): $t_R = 14.5$ (major), 20.5 (minor).

(S)-2-(1-(4-Chlorophenyl)-2-oxopentyl)cyclohex-2-en-1-one (3fa)

The title compound was isolated through column chromatography (silica gel, petroleum ether/ethyl acetate = 5:1) as a colorless oil (24.2 mg, 47% yield).

¹**H NMR** (500 MHz, Chloroform-*d*) δ = 7.67 (d, J = 8.1 Hz, 2H), 7.40 – 7.34 (m, 3H), 4.46 – 4.37 (m, 1H), 3.22 (dd, J = 16.8, 5.0 Hz, 1H), 2.71 – 2.63 (m, 1H), 2.58 (dd, J = 16.8, 9.1 Hz, 1H), 2.26 (dd, J = 12.5, 6.7 Hz, 1H), 1.47 (dd, J = 12.6, 8.8 Hz, 1H), 1.35 (s, 3H), 1.33 (s, 3H), 1.14 (d, J = 6.8 Hz, 3H), 1.12 (d, J = 6.9 Hz, 3H) ppm.

¹³C NMR (126 MHz, Chloroform-*d*) δ = 213.6, 180.1, 134.7, 129.6, 128.3 (2C), 128.0 (2C), 64.2, 50.8, 48.8, 47.4, 41.4, 27.4, 26.0, 18.3, 18.2 ppm.

HRMS (ESI) m/z calculated for $C_{17}H_{23}NONa^+$ [M+Na]⁺: 280.1672, found: 280.1676. **HPLC-Data**: 98% *ee*, (Chiral MD column, $\lambda = 254$ nm, hexane/isopropanol = 95/5, flow rate = 0.5 mL/min): $t_R = 10.6$ (major), 11.6 (minor).

(S)-1-Cyclohexyl-2-(4,4-dimethyl-5-phenyl-3,4-dihydro-2*H*-pyrrol-2-yl)ethan-1-one (3ga)

The title compound was isolated through column chromatography (silica gel, petroleum ether/ethyl acetate = 5:1) as a colorless oil (27.3 mg, 46% yield).

¹**H NMR** (400 MHz, Chloroform-*d*) δ = 7.67 (d, J = 7.9 Hz, 2H), 7.42 – 7.32 (m, 3H), 4.47 – 4.33 (m, 1H), 3.20 (dd, J = 16.9, 4.9 Hz, 1H), 2.56 (dd, J = 16.9, 9.2 Hz, 1H), 2.45 – 2.35 (m, 1H), 2.25 (dd, J = 12.6, 6.7 Hz, 1H), 1.93 – 1.84 (m, 2H), 1.82 – 1.75 (m, 2H), 1.70 – 1.62 (m, 1H), 1.46 (dd, J = 12.6, 8.8 Hz, 1H), 1.35 (s, 3H), 1.33 (s, 3H), 1.39 – 1.18 (m, 5H) ppm.

¹³C NMR (101 MHz, Chloroform-*d*) δ = 213.0, 180.0, 134.8, 129.6, 128.3 (2C), 128.0 (2C), 64.2, 51.3, 50.8, 48.8, 47.8, 28.52, 28.46, 27.5, 26.0 (2C), 25.82, 25.77 ppm.

HRMS (ESI) m/z calculated for C₂₀H₂₇NOH⁺ [M+H]⁺: 298.2165, found: 298.2174.

HPLC-Data: 92% *ee*, (Chiralpak IA column, $\lambda = 254$ nm, hexane/isopropanol = 90/10, flow rate = 0.5 mL/min): $t_R = 10.9$ (major), 13.2 (minor).

(S)-2-(4,4-Dimethyl-5-phenyl-3,4-dihydro-2*H*-pyrrol-2-yl)-1-phenylethan-1-one (3ha)

The title compound was isolated through column chromatography (silica gel, petroleum ether/ethyl acetate = 5:1) as a colorless oil (34.3 mg, 59% yield).

¹**H NMR** (400 MHz, Chloroform-*d*) δ = 8.02 (d, *J* = 8.6 Hz, 2H), 7.69 (d, *J* = 7.9 Hz, 2H), 7.58 (t, *J* = 7.3 Hz, 1H), 7.48 (t, *J* = 7.7 Hz, 2H), 7.42 – 7.35 (m, 3H), 4.66 – 4.55 (m, 1H), 3.84 (dd, *J* = 16.8, 4.5 Hz, 1H), 3.06 (dd, *J* = 16.8, 9.5 Hz, 1H), 2.35 (dd, *J* = 12.7, 6.8 Hz, 1H), 1.60 (dd, *J* = 12.7, 8.7 Hz, 1H), 1.38 (s, 3H), 1.36 (s, 3H) ppm.

¹³C NMR (101 MHz, Chloroform-*d*) δ = 198.9, 180.3, 137.2, 134.8, 133.3, 129.6, 128.7

(2C), 128.33 (2C), 128.31 (2C), 128.0 (2C), 64.5, 50.9, 48.8, 46.0, 27.5, 26.0 ppm. **HRMS** (ESI) m/z calculated for $C_{20}H_{21}NOH^+$ [M+H]⁺: 292.1696, found: 292.1699. **HPLC-Data**: 92% *ee*, (Chiral MD column, $\lambda = 254$ nm, hexane/isopropanol = 95/5, flow rate = 0.5 mL/min): $t_R = 15.8$ (major), 18.0 (minor).

(S)-2-(4,4-Dimethyl-5-phenyl-3,4-dihydro-2*H*-pyrrol-2-yl)-1-(*p*-tolyl)ethan-1-one (3ia)

The title compound was isolated through column chromatography (silica gel, petroleum ether/ethyl acetate = 5:1) as a colorless oil (38.3 mg, 63% yield).

¹**H NMR** (400 MHz, Chloroform-*d*) δ = 7.93 (d, J = 8.2 Hz, 2H), 7.69 (d, J = 7.8 Hz, 2H), 7.41 – 7.35 (m, 3H), 7.28 (d, J = 7.9 Hz, 2H), 4.64 – 4.54 (m, 1H), 3.82 (dd, J = 16.6, 4.4 Hz, 1H), 3.03 (dd, J = 16.7, 9.6 Hz, 1H), 2.42 (s, 3H), 2.34 (dd, J = 12.7, 6.7 Hz, 1H), 1.59 (dd, J = 12.7, 8.7 Hz, 1H), 1.37 (s, 3H), 1.36 (s, 3H) ppm.

¹³C NMR (101 MHz, Chloroform-*d*) δ = 198.6, 180.2, 144.0, 134.8, 134.7, 129.6, 129.4 (2C), 128.4 (2C), 128.3 (2C), 128.0 (2C), 64.6, 50.9, 48.8, 45.9, 27.5, 26.0, 21.8 ppm. **HRMS** (ESI) m/z calculated for C₂₁H₂₃NOH⁺ [M+H]⁺: 306.1852, found: 306.1856.

HPLC-Data: 97% *ee*, (Chiral MD column, $\lambda = 254$ nm, hexane/isopropanol = 92/8, flow rate = 0.5 mL/min): $t_R = 11.9$ (major), 15.5 (minor).

(S)-1-(4-(tert-Butyl)phenyl)-2-(4,4-dimethyl-5-phenyl-3,4-dihydro-2H-pyrrol-2-yl)ethan-1-one (3ja)

The title compound was isolated through column chromatography (silica gel, petroleum ether/ethyl acetate = 6:1) as a colorless oil (49.3 mg, 71% yield).

¹**H NMR** (400 MHz, Chloroform-d) $\delta = 7.97$ (d, J = 8.5 Hz, 2H), 7.69 (d, J = 7.9 Hz,

2H), 7.49 (d, J = 8.5 Hz, 2H), 7.41 – 7.35 (m, 3H), 4.66 – 4.54 (m, 1H), 3.83 (dd, J = 16.7, 4.3 Hz, 1H), 3.04 (dd, J = 16.7, 9.7 Hz, 1H), 2.35 (dd, J = 12.7, 6.7 Hz, 1H), 1.59 (dd, J = 12.7, 8.6 Hz, 1H), 1.37 (s, 3H), 1.35 (s, 3H), 1.35 (s, 9H) ppm.

¹³C NMR (101 MHz, Chloroform-*d*) δ = 198.6, 180.3, 157.0, 134.8, 134.6, 129.6, 128.3 (4C), 128.0 (2C), 125.7 (2C), 64.6, 50.9, 48.8, 46.0, 35.2, 31.2 (3C), 27.5, 26.1 ppm.

HRMS (ESI) m/z calculated for C₂₄H₂₉NONa⁺ [M+Na]⁺: 370.2141, found: 370.2147.

HPLC-Data: 93% *ee*, (Chiral MD column, $\lambda = 254$ nm, hexane/isopropanol = 95/5, flow rate = 0.5 mL/min): $t_R = 16.9$ (major), 22.4 (minor).

(S)-2-(4,4-Dimethyl-5-phenyl-3,4-dihydro-2*H*-pyrrol-2-yl)-1-(4-fluorophenyl)-ethan-1-one (3ka)

The title compound was isolated through column chromatography (silica gel, petroleum ether/ethyl acetate = 5:1) as a colorless oil (43.2 mg, 70% yield).

¹**H NMR** (400 MHz, Chloroform-*d*) δ = 8.09 – 8.01 (m, 2H), 7.68 (d, J = 7.9 Hz, 2H), 7.43 – 7.34 (m, 3H), 7.18 – 7.11 (m, 2H), 4.63 – 4.52 (m, 1H), 3.78 (dd, J = 16.7, 4.6 Hz, 1H), 3.03 (dd, J = 16.7, 9.2 Hz, 1H), 2.34 (dd, J = 12.6, 6.7 Hz, 1H), 1.59 (dd, J = 12.7, 8.8 Hz, 1H), 1.38 (s, 3H), 1.36 (s, 3H) ppm.

¹³C NMR (101 MHz, Chloroform-*d*) δ = 197.4, 180.4, 165.9 (d, *J* = 254.8 Hz), 134.7, 133.6 (d, *J* = 3.0 Hz), 131.0 (d, *J* = 9.3 Hz, 2C), 129.7, 128.3 (2C), 128.0 (2C), 115.8 (d, *J* = 21.9 Hz, 2C), 64.5, 50.9, 48.8, 45.9, 27.5, 26.0 ppm.

¹⁹**F NMR** (376 MHz, Chloroform-*d*) δ = –105.21 (s, 1F) ppm.

HRMS (ESI) m/z calculated for $C_{20}H_{20}FNONa^+$ [M+Na]⁺: 332.1421, found: 332.1422. **HPLC-Data**: 92% *ee*, (Chiral MD column, $\lambda = 254$ nm, hexane/isopropanol = 95/5, flow rate = 0.5 mL/min): $t_R = 14.7$ (major), 22.4 (minor).

(S)-4-(2-(4,4-Dimethyl-5-phenyl-3,4-dihydro-2*H*-pyrrol-2-yl)acetyl)phenyl acetate (3la)

The title compound was isolated through column chromatography (silica gel, petroleum ether/ethyl acetate = 3:1) as a colorless oil (51.6 mg, 74% yield).

¹**H NMR** (500 MHz, Chloroform-*d*) δ = 8.06 (d, J = 8.7 Hz, 2H), 7.68 (d, J = 8.1 Hz, 2H), 7.42 – 7.35 (m, 3H), 7.20 (d, J = 8.7 Hz, 2H), 4.66 – 4.57 (m, 1H), 3.83 (dd, J = 16.7, 4.5 Hz, 1H), 3.04 (dd, J = 16.8, 9.5 Hz, 1H), 2.36 (dd, J = 12.6, 6.7 Hz 1H), 2.33 (s, 3H), 1.60 (dd, J = 12.7, 8.7 Hz, 1H), 1.38 (s, 3H), 1.36 (s, 3H) ppm.

¹³C NMR (126 MHz, Chloroform-*d*) δ = 197.6, 180.8, 169.0, 154.5, 134.7, 134.6, 130.0 (2C), 129.8, 128.4 (2C), 128.0 (2C), 122.0 (2C), 64.4, 51.0, 48.6, 45.9, 27.5, 26.0, 21.3 ppm.

HRMS (ESI) m/z calculated for $C_{22}H_{23}NO_3H^+$ [M+H]⁺: 350.1751, found: 350.1757. **HPLC-Data**: 94% *ee*, (Chiral MD column, $\lambda = 254$ nm, hexane/isopropanol = 90/10, flow rate = 0.5 mL/min): $t_R = 22.7$ (minor), 24.5 (major).

(S)-N-(4-(2-(4,4-Dimethyl-5-phenyl-3,4-dihydro-2*H*-pyrrol-2-yl)acetyl)phenyl)-acetamide (3ma)

The title compound was isolated through column chromatography (silica gel, petroleum ether/ethyl acetate = 1:1) as a white solid (32.0 mg, 46% yield).

¹**H NMR** (400 MHz, Chloroform-*d*) δ = 7.93 (d, J = 8.4 Hz, 2H), 7.66 (d, J = 7.9 Hz, 2H), 7.59 (d, J = 8.4 Hz, 2H), 7.43 – 7.32 (m, 3H), 4.66 – 4.56 (m, 1H), 3.73 (dd, J = 16.6, 5.1 Hz, 1H), 3.01 (dd, J = 16.6, 8.8 Hz, 1H), 2.32 (dd, J = 12.6, 6.7 Hz, 1H), 2.14 (s, 3H), 1.61 (dd, J = 12.7, 8.8 Hz, 1H), 1.37 (s, 3H), 1.35 (s, 3H) ppm.

¹³C **NMR** (101 MHz, Chloroform-*d*) $\delta = 197.6$, 180.7, 168.8, 142.6, 134.7, 132.7,

129.69 (2C), 129.73 (2C), 128.4 (2C), 127.9 (2C), 119.0, 64.5, 50.9, 48.6, 45.7, 27.4, 26.0, 24.8 ppm.

HRMS (ESI) m/z calculated for $C_{22}H_{24}N_2O_2H^+$ [M+H]⁺: 349.1911, found: 349.1921. **HPLC-Data**: 90% *ee*, (Chiral MD column, $\lambda = 254$ nm, hexane/isopropanol = 80/20, flow rate = 0.5 mL/min): $t_R = 11.9$ (major), 14.3 (minor).

(S)-2-(4,4-Dimethyl-5-phenyl-3,4-dihydro-2*H*-pyrrol-2-yl)-1-(4-(pyridin-2-yl)-phenyl)ethan-1-one (3na)

The title compound was isolated through column chromatography (silica gel, petroleum ether/ethyl acetate = 2:1) as a white solid (28.7 mg, 39% yield).

¹**H NMR** (400 MHz, Chloroform-*d*) δ = 8.74 (d, J = 4.8 Hz, 1H), 8.17 – 8.09 (m, 4H), 7.80 (d, J = 4.5 Hz, 2H), 7.70 (d, J = 7.8 Hz, 2H), 7.43 – 7.35 (m, 3H), 7.33 – 7.27 (m, 1H), 4.68 – 4.58 (m, 1H), 3.89 (dd, J = 16.8, 4.5 Hz, 1H), 3.10 (dd, J = 16.7, 9.4 Hz, 1H), 2.37 (dd, J = 12.7, 6.7 Hz, 1H), 1.63 (dd, J = 12.7, 8.8 Hz, 1H), 1.39 (s, 3H), 1.37 (s, 3H) ppm.

¹³C **NMR** (101 MHz, Chloroform-*d*) $\delta = 198.6$, 180.4, 156.2, 150.1, 143.7, 137.2, 137.1, 134.8, 129.7, 128.9 (2C), 128.3 (2C), 128.0 (2C), 127.2 (2C), 123.1, 121.2, 64.5, 51.0, 48.8, 46.2, 27.5, 26.0 ppm.

HRMS (ESI) m/z calculated for $C_{25}H_{24}N_2OH^+$ [M+H]⁺: 369.1961, found: 369.1972. **HPLC-Data**: 97% *ee*, (Chiral MD column, $\lambda = 254$ nm, hexane/isopropanol = 80/20, flow rate = 0.5 mL/min): $t_R = 24.4$ (major), 32.9 (minor).

(S)-2-(4,4-Dimethyl-5-phenyl-3,4-dihydro-2*H*-pyrrol-2-yl)-1-(4-(trifluoromethyl)-phenyl)ethan-1-one (30a)

The title compound was isolated through column chromatography (silica gel, petroleum ether/ethyl acetate = 5:1) as a colorless oil (24.2 mg, 34% yield).

¹**H NMR** (400 MHz, Chloroform-*d*) δ = 8.12 (d, J = 8.1 Hz, 2H), 7.75 (d, J = 8.2 Hz, 2H), 7.67 (d, J = 8.0 Hz, 2H), 7.42 – 7.34 (m, 3H), 4.66 – 4.53 (m, 1H), 3.80 (dd, J = 16.8, 4.9 Hz, 1H), 3.09 (dd, J = 16.8, 8.9 Hz, 1H), 2.35 (dd, J = 12.7, 6.7 Hz, 1H), 1.61 (dd, J = 12.7, 8.8 Hz, 1H), 1.39 (s, 3H), 1.36 (s, 3H) ppm.

¹³C **NMR** (101 MHz, Chloroform-*d*) δ = 198.0, 180.5, 139.9, 134.7, 134.5 (q, J = 32.7 Hz), 129.8, 128.7 (2C), 128.4 (2C), 128.0 (2C), 125.8 (q, J = 3.8 Hz, 2C), 123.8 (q, J = 272.7 Hz), 64.4, 51.0, 48.8, 46.3, 27.5, 26.0 ppm.

¹⁹**F NMR** (376 MHz, Chloroform-*d*) δ = –63.09 (s, 3F) ppm.

HRMS (ESI) m/z calculated for $C_{21}H_{20}F_3NOH^+$ [M+H]⁺: 360.1570, found: 360.1582. **HPLC-Data**: 77% *ee*, (Chiral MD column, $\lambda = 254$ nm, hexane/isopropanol = 90/10, flow rate = 0.5 mL/min): $t_R = 12.2$ (major), 23.0 (minor).

Methyl (S)-3-(2-(4,4-dimethyl-5-phenyl-3,4-dihydro-2*H*-pyrrol-2-yl)acetyl)-benzoate (3pa)

The title compound was isolated through column chromatography (silica gel, petroleum ether/ethyl acetate = 3:1) as a yellow oil (38.4 mg, 55% yield).

¹**H NMR** (400 MHz, Chloroform-*d*) δ = 8.67 (s, 1H), 8.28 – 8.18 (m, 2H), 7.69 (d, J = 7.8 Hz, 2H), 7.57 (t, J = 7.8 Hz, 1H), 7.43 – 7.33 (m, 3H), 4.66 – 4.55 (m, 1H), 3.96 (s, 3H), 3.84 (dd, J = 16.7, 4.9 Hz, 1H), 3.10 (dd, J = 16.8, 9.0 Hz, 1H), 2.35 (dd, J = 12.7, 6.7 Hz, 1H), 1.61 (dd, J = 12.6, 8.8 Hz, 1H), 1.39 (s, 3H), 1.37 (s, 3H) ppm.

¹³C NMR (101 MHz, Chloroform-*d*) $\delta = 198.2$, 180.4, 166.4, 137.5, 134.7, 134.1, 132.4, 130.9, 129.7, 129.6, 129.0, 128.3 (2C), 128.0 (2C), 64.5, 52.5, 51.0, 48.8, 46.1, 27.5, 26.0 ppm.

HRMS (ESI) m/z calculated for $C_{22}H_{23}NO_3Na^+$ [M+Na]⁺: 372.1570, found: 372.1570. **HPLC-Data**: 56% *ee*, (Chiral MD column, $\lambda = 254$ nm, hexane/isopropanol = 80/20, flow rate = 0.5 mL/min): $t_R = 10.7$ (major), 12.4 (minor).

(S)-2-(4,4-Dimethyl-5-phenyl-3,4-dihydro-2*H*-pyrrol-2-yl)-1-(3-fluorophenyl)-ethan-1-one (3qa)

The title compound was isolated through column chromatography (silica gel, petroleum ether/ethyl acetate = 5:1) as a colorless oil (24.1 mg, 39% yield).

¹**H NMR** (400 MHz, Chloroform-*d*) δ = 7.81 (d, J = 7.8 Hz, 1H), 7.73 – 7.66 (m, 3H), 7.50 – 7.43 (m, 1H), 7.42 – 7.34 (m, 3H), 7.30 – 7.25 (m, 1H), 4.64 – 4.54 (m, 1H), 3.78 (dd, J = 16.8, 4.7 Hz, 1H), 3.04 (dd, J = 16.8, 9.1 Hz, 1H), 2.35 (dd, J = 12.6, 6.7 Hz, 1H), 1.59 (dd, J = 12.7, 8.8 Hz, 1H), 1.38 (s, 3H), 1.36 (s, 3H) ppm.

¹³C NMR (101 MHz, Chloroform-*d*) $\delta = 197.7$ (d, J = 2.1 Hz), 180.5, 163.0 (d, J = 247.7 Hz), 139.3 (d, J = 6.1 Hz), 134.7, 130.4 (d, J = 7.6 Hz), 129.7, 128.3 (2C), 128.0 (2C), 124.1 (d, J = 3.0 Hz), 120.3 (d, J = 21.5 Hz), 115.1 (d, J = 22.3 Hz), 64.4, 51.0, 48.8, 46.2, 27.5, 26.0 ppm.

¹⁹**F NMR** (376 MHz, Chloroform-*d*) δ = –111.84 (s, 1F) ppm.

HRMS (ESI) m/z calculated for $C_{20}H_{20}FNONa^{+}$ [M+Na]⁺: 332.1421, found: 332.1427. **HPLC-Data**: 87% *ee*, (Chiral MD column, $\lambda = 254$ nm, hexane/isopropanol = 95/5, flow rate = 0.5 mL/min): $t_R = 14.3$ (major), 18.0 (minor).

(S)-2-(4,4-Dimethyl-5-phenyl-3,4-dihydro-2*H*-pyrrol-2-yl)-1-(*m*-tolyl)ethan-1-one (3ra)

The title compound was isolated through column chromatography (silica gel, petroleum ether/ethyl acetate = 5:1) as a colorless oil (28.7 mg, 47% yield).

¹**H NMR** (400 MHz, Chloroform-*d*) δ = 7.86 – 7.80 (m, 2H), 7.69 (d, *J* = 7.9 Hz, 2H), 7.41 – 7.34 (m, 5H), 4.67 – 4.53 (m, 1H), 3.83 (dd, *J* = 16.7, 4.4 Hz, 1H), 3.04 (dd, *J* = 16.7, 9.6 Hz, 1H), 2.42 (s, 3H), 2.34 (dd, *J* = 12.7, 6.8 Hz, 1H), 1.59 (dd, *J* = 12.7, 8.7 Hz, 1H), 1.38 (s, 3H), 1.36 (s, 3H) ppm.

¹³C **NMR** (101 MHz, Chloroform-*d*) $\delta = 199.2$, 180.3, 138.5, 137.2, 134.8, 134.0, 129.6, 128.9, 128.6, 128.3 (2C), 128.0 (2C), 125.6, 64.6, 50.9, 48.8, 46.2, 27.5, 26.1, 21.5 ppm.

HRMS (ESI) m/z calculated for $C_{21}H_{23}NONa^+$ [M+Na]⁺: 306.1852, found: 306.1861. **HPLC-Data**: 96% *ee*, (Chiralpak IA column, $\lambda = 254$ nm, hexane/isopropanol = 70/30, flow rate = 1.0 mL/min): $t_R = 4.1$ (major), 4.7 (minor).

(S)-2-(4,4-Dimethyl-5-phenyl-3,4-dihydro-2*H*-pyrrol-2-yl)-1-(*o*-tolyl)ethan-1-one (3sa)

The title compound was isolated through column chromatography (silica gel, petroleum ether/ethyl acetate = 5:1) as a colorless oil (36.0 mg, 59% yield).

¹**H NMR** (500 MHz, Chloroform-*d*) δ = 7.74 (d, J = 7.8 Hz, 1H), 7.69 (d, J = 8.0 Hz, 2H), 7.40 – 7.35 (m, 4H), 7.29 – 7.25 (m, 2H), 4.60 – 4.53 (m, 1H), 3.73 (dd, J = 16.5, 4.9 Hz, 1H), 3.00 (dd, J = 16.6, 9.3 Hz, 1H), 2.54 (s, 3H), 2.33 (dd, J = 12.6, 6.7 Hz, 1H), 1.59 (dd, J = 12.6, 8.7 Hz, 1H), 1.38 (s, 3H), 1.36 (s, 3H) ppm.

¹³C **NMR** (126 MHz, Chloroform-*d*) $\delta = 203.0$, 180.1, 138.4, 138.0, 134.8, 132.1,

131.5, 129.6, 128.9, 128.3 (2C), 128.0 (2C), 125.9, 64.7, 50.9, 48.9, 48.8, 27.5, 26.1, 21.6 ppm.

HRMS (ESI) m/z calculated for $C_{21}H_{23}NOH^+$ [M+H]⁺: 306.1852, found: 306.1861. **HPLC-Data**: 90% *ee*, (Chiral MD column, $\lambda = 254$ nm, hexane/isopropanol = 95/5,

flow rate = 0.5 mL/min): $t_R = 15.7 \text{ (major)}, 18.0 \text{ (minor)}.$

(S)-2-(4,4-Dimethyl-5-phenyl-3,4-dihydro-2*H*-pyrrol-2-yl)-1-(2-methoxyphenyl)-ethan-1-one (3ta)

The title compound was isolated through column chromatography (silica gel, petroleum ether/ethyl acetate = 3:1) as a colorless oil (28.3 mg, 44% yield).

¹**H NMR** (400 MHz, Chloroform-*d*) δ = 7.75 (d, J = 7.7 Hz, 1H), 7.68 (d, J = 7.7 Hz, 2H), 7.46 (t, J = 7.9 Hz, 1H), 7.40 – 7.35 (m, 3H), 7.05 – 6.95 (m, 2H), 4.62 – 4.53 (m, 1H), 3.91 (s, 3H), 3.85 (dd, J = 17.1, 4.3 Hz, 1H), 3.11 (dd, J = 17.4, 9.7 Hz, 1H), 2.32 (dd, J = 12.7, 6.8 Hz, 1H), 1.57 (dd, J = 12.7, 8.6 Hz, 1H), 1.36 (s, 3H), 1.34 (s, 3H) ppm.

¹³C **NMR** (101 MHz, Chloroform-*d*) $\delta = 201.0$, 180.0, 158.8, 135.0, 133.6, 130.5, 129.5, 128.5, 128.3 (2C), 128.0 (2C), 120.7, 111.6, 64.7, 55.6, 51.3, 50.8, 48.7, 27.5, 26.1 ppm.

HRMS (ESI) m/z calculated for $C_{21}H_{23}NO_2H^+$ [M+H]⁺: 322.1802, found: 322.1807.

HPLC-Data: 92% *ee*, (Chiral MD column, $\lambda = 254$ nm, hexane/isopropanol = 90/10, flow rate = 0.5 mL/min): $t_R = 15.5$ (major), 17.2 (minor).

(S)-2-(4,4-Dimethyl-5-phenyl-3,4-dihydro-2*H*-pyrrol-2-yl)-1-(naphthalen-1-yl)-ethan-1-one (3ua)

The title compound was isolated through column chromatography (silica gel, petroleum ether/ethyl acetate = 4:1) as a colorless oil (22.5 mg, 33% yield).

¹**H NMR** (400 MHz, Chloroform-*d*) δ = 8.68 (d, J = 8.5 Hz, 1H), 8.00 (m, 2H), 7.89 (d, J = 8.1 Hz, 1H), 7.69 (d, J = 8.0 Hz, 2H), 7.61 (t, J = 7.8 Hz, 1H), 7.57 – 7.50 (m, 2H), 7.42 – 7.35 (m, 3H), 4.70 – 4.61 (m, 1H), 3.90 (dd, J = 16.3, 5.0 Hz, 1H), 3.15 (dd, J = 16.3, 9.2 Hz, 1H), 2.36 (dd, J = 12.6, 6.7 Hz, 1H), 1.67 (dd, J = 12.6, 8.8 Hz, 1H), 1.39 (s, 3H), 1.37 (s, 3H) ppm.

¹³C **NMR** (101 MHz, Chloroform-*d*) $\delta = 203.3$, 180.2, 136.1, 134.7, 134.1, 132.9, 130.3, 129.7, 128.6, 128.3 (2C), 128.1 (2C), 128.0 (2C), 126.6, 126.0, 124.6, 64.9, 51.0, 49.4, 48.7, 27.5, 26.1 ppm.

HRMS (ESI) m/z calculated for $C_{24}H_{23}NONa^+$ [M+Na]⁺: 364.1672, found: 364.1674. **HPLC-Data**: 97% *ee*, (Chiral MD column, $\lambda = 254$ nm, hexane/isopropanol = 90/10, flow rate = 0.5 mL/min): $t_R = 16.3$ (major), 20.9 (minor).

(S)-2-(4,4-Dimethyl-5-phenyl-3,4-dihydro-2*H*-pyrrol-2-yl)-1-(naphthalen-2-yl)-ethan-1-one (3va)

The title compound was isolated through column chromatography (silica gel, petroleum ether/ethyl acetate = 5:1) as a colorless oil (38.2 mg, 56% yield).

¹**H NMR** (400 MHz, Chloroform-*d*) δ = 8.57 (s, 1H), 8.10 (d, *J* = 8.6 Hz, 1H), 7.98 (d, *J* = 7.5 Hz, 1H), 7.93 – 7.87 (m, 2H), 7.71 (d, *J* = 7.9 Hz, 2H), 7.63 – 7.54 (m, 2H), 7.42 – 7.35 (m, 3H), 4.71 – 4.61 (m, 1H), 3.99 (dd, *J* = 16.5, 4.5 Hz, 1H), 3.19 (dd, *J* =

16.5, 9.5 Hz, 1H), 2.38 (dd, J = 12.7, 6.7 Hz, 1H), 1.66 (dd, J = 12.7, 8.7 Hz, 1H), 1.40 (s, 3H), 1.38 (s, 3H) ppm.

¹³C **NMR** (101 MHz, Chloroform-*d*) $\delta = 198.9$, 180.3, 135.7, 134.8, 134.5, 132.7, 130.2, 129.8, 129.7, 128.62, 128.59, 128.3 (2C), 128.0 (2C), 127.9, 126.9, 124.0, 64.7, 51.0, 48.8, 46.2, 27.5, 26.1 ppm.

HRMS (ESI) m/z calculated for $C_{24}H_{23}NONa^+$ [M+Na]⁺: 364.1672, found: 364.1676. **HPLC-Data**: 96% *ee*, (Chiral MD column, $\lambda = 254$ nm, hexane/isopropanol = 90/10, flow rate = 0.5 mL/min): $t_R = 17.4$ (minor), 23.0 (major).

(S)-2-(4,4-Dimethyl-5-phenyl-3,4-dihydro-2*H*-pyrrol-2-yl)-1-(thiophen-3-yl)-ethan-1-one (3wa)

The title compound was isolated through column chromatography (silica gel, petroleum ether/ethyl acetate = 4:1) as a yellow oil (29.1 mg, 49% yield).

¹**H NMR** (400 MHz, Chloroform-*d*) $\delta = 8.16 - 8.10$ (m, 1H), 7.68 (d, J = 7.9 Hz, 2H), 7.59 (d, J = 5.1 Hz, 1H), 7.42 – 7.35 (m, 3H), 7.35 – 7.31 (m, 1H), 4.62 – 4.51 (m, 1H), 3.73 (dd, J = 16.3, 4.6 Hz, 1H), 2.98 (dd, J = 16.3, 9.5 Hz, 1H), 2.33 (dd, J = 12.7, 6.7 Hz, 1H), 1.61 (dd, J = 12.7, 8.8 Hz, 1H), 1.37 (s, 3H), 1.36 (s, 3H) ppm.

¹³C NMR (101 MHz, Chloroform-*d*) δ = 193.3, 180.4, 142.6, 134.7, 132.5, 129.7, 128.3 (2C), 128.0 (2C), 127.1, 126.5, 64.5, 51.0, 48.7, 47.2, 27.5, 26.0 ppm.

HRMS (ESI) m/z calculated for $C_{18}H_{19}NOSNa^+$ [M+Na]⁺: 320.1080, found: 320.1086. **HPLC-Data**: 95% *ee*, (Chiral MD column, $\lambda = 254$ nm, hexane/isopropanol = 90/10, flow rate = 0.5 mL/min): $t_R = 14.5$ (minor), 15.4 (major).

(S)-2-(4,4-Dimethyl-5-phenyl-3,4-dihydro-2*H*-pyrrol-2-yl)-1-(furan-3-yl)ethan-1-one (3xa)

The title compound was isolated through column chromatography (silica gel, petroleum ether/ethyl acetate = 3:1) as a colorless oil (19.6 mg, 35% yield).

¹**H NMR** (400 MHz, Chloroform-*d*) δ = 8.11 (s, 1H), 7.74 (d, J = 7.2 Hz, 2H), 7.49 – 7.35 (m, 4H), 6.81 (s, 1H), 4.64 – 4.51 (m, 1H), 3.65 (dd, J = 15.9, 4.5 Hz, 1H), 2.88 (dd, J = 16.1, 9.3 Hz, 1H), 2.34 (dd, J = 12.7, 6.7 Hz, 1H), 1.65 (dd, J = 12.7, 8.9 Hz, 1H), 1.40 (s, 3H), 1.38 (s, 3H) ppm.

¹³C NMR (101 MHz, Chloroform-*d*) δ = 193.4, 181.3, 147.8, 144.4, 133.7, 130.4, 128.5 (2C), 128.3 (2C), 128.1, 108.7, 63.9, 50.9, 48.4, 47.3, 27.4, 26.1 ppm.

HRMS (ESI) m/z calculated for $C_{18}H_{19}NO_2Na^+$ [M+Na]⁺: 304.1308, found: 304.1314. **HPLC-Data**: 99% *ee*, (Chiralpak AD-H column, $\lambda = 254$ nm, hexane/isopropanol = 90/10, flow rate = 0.5 mL/min): $t_R = 13.1$ (major), 15.9 (minor).

(S)-2-(4,4-Dimethyl-5-phenyl-3,4-dihydro-2*H*-pyrrol-2-yl)-1-(1-ethyl-1*H*-pyrazol-4-yl)ethan-1-one (3ya)

The title compound was isolated through column chromatography (silica gel, petroleum ether/ethyl acetate = 1:1) as a yellow oil (26.6 mg, 43% yield).

¹**H NMR** (400 MHz, Chloroform-*d*) δ = 7.98 – 7.94 (m, 2H), 7.70 – 7.64 (m, 2H), 7.41 – 7.33 (m, 3H), 4.57 – 4.48 (m, 1H), 4.20 (q, *J* = 7.3 Hz, 2H), 3.53 (dd, *J* = 15.7, 5.0 Hz, 1H), 2.84 (dd, *J* = 15.7, 9.2 Hz, 1H), 2.28 (dd, *J* = 12.7, 6.7 Hz, 1H), 1.61 (dd, *J* = 12.7, 8.8 Hz, 1H), 1.52 (t, *J* = 7.3 Hz, 3H), 1.36 (s, 3H), 1.34 (s, 3H) ppm.

¹³C NMR (101 MHz, Chloroform-*d*) δ = 193.2, 180.3, 140.5, 134.8, 131.1, 129.7, 128.3 (2C), 128.0 (2C), 124.2, 64.6, 50.9, 48.6, 47.68, 47.65, 27.4, 26.0, 15.3 ppm.

HRMS (ESI) m/z calculated for $C_{19}H_{23}N_3OH^+$ [M+H]⁺: 310.1914, found: 310.1924. **HPLC-Data**: 90% *ee*, (Chiral MD column, $\lambda = 254$ nm, hexane/isopropanol = 80/20, flow rate = 0.5 mL/min): $t_R = 12.0$ (minor), 14.2 (major).

(S)-1-(1-Phenyl-2-azaspiro[4.4]non-1-en-3-yl)pentan-2-one (3ab)

The title compound was isolated through column chromatography (silica gel, petroleum ether/ethyl acetate = 5:1) as a colorless oil (29.5 mg, 52% yield).

¹**H NMR** (500 MHz, Chloroform-*d*) δ = 7.62 (d, J = 7.9 Hz, 2H), 7.40 – 7.33 (m, 3H), 4.41 – 4.33 (m, 1H), 3.13 (dd, J = 16.4, 5.3 Hz, 1H), 2.54 (dd, J = 16.4, 8.8 Hz, 1H), 2.51 – 2.41 (m, 2H), 2.32 (dd, J = 12.5, 6.7 Hz, 1H), 2.24 – 2.14 (m, 1H), 1.91 – 1.84 (m, 1H), 1.84 – 1.75 (m, 3H), 1.74 – 1.68 (m, 2H), 1.67 – 1.60 (m, 2H), 1.56 – 1.50 (m, 1H), 1.42 (dd, J = 12.5, 8.4 Hz, 1H), 0.93 (t, J = 7.4 Hz, 3H) ppm.

¹³C NMR (126 MHz, Chloroform-*d*) δ = 210.2, 179.5, 134.6, 129.6, 128.3 (2C), 128.0 (2C), 64.8, 61.1, 49.7, 48.5, 45.6, 37.9, 36.2, 25.8, 25.3, 17.3, 13.9 ppm.

HRMS (ESI) m/z calculated for $C_{19}H_{25}NONa^+$ [M+Na]⁺: 306.1828, found: 306.1829. **HPLC-Data**: 96% *ee*, (Chiral MD column, $\lambda = 254$ nm, hexane/isopropanol = 95/5, flow rate = 0.5 mL/min): $t_R = 13.8$ (minor), 16.3 (major).

(S)-1-(1-Phenyl-2-azaspiro[4.5]dec-1-en-3-yl)pentan-2-one (3ac)

The title compound was isolated through column chromatography (silica gel, petroleum ether/ethyl acetate = 4:1) as a colorless oil (44.6 mg, 75% yield).

¹**H NMR** (400 MHz, Chloroform-*d*) δ = 7.51 (d, J = 7.5 Hz, 2H), 7.41 – 7.31 (m, 3H), 4.46 – 4.35 (m, 1H), 3.13 (dd, J = 16.5, 5.1 Hz, 1H), 2.59 – 2.42 (m, 4H), 1.84 – 1.75 (m, 1H), 1.73 – 1.55 (m, 7H), 1.51 – 1.41 (m, 2H), 1.33 (dd, J = 13.0, 8.6 Hz, 1H), 1.29 – 1.22 (m, 1H), 1.20 – 1.10 (m, 1H), 0.93 (t, J = 7.4 Hz, 3H) ppm.

¹³C NMR (101 MHz, Chloroform-*d*) δ = 210.0, 181.1, 135.7, 129.1, 128.1 (4C), 64.9,

56.8, 50.2, 45.6, 41.7, 36.0, 31.8, 25.7, 23.4, 23.2, 17.3, 13.9 ppm.

HRMS (ESI) m/z calculated for C₂₀H₂₇NOH⁺ [M+H]⁺: 298.2165, found: 298.2169.

HPLC-Data: 95% *ee*, (Chiral MD column, $\lambda = 254$ nm, hexane/isopropanol = 90/10, flow rate = 0.5 mL/min): $t_R = 11.1$ (minor), 12.0 (major).

(S)-1-(5-Phenyl-3,4-dihydro-2*H*-pyrrol-2-yl)pentan-2-one (3ad)

The title compound was isolated through column chromatography (silica gel, petroleum ether/ethyl acetate = 4:1) as a yellow oil (11.0 mg, 24% yield).

¹**H NMR** (400 MHz, Chloroform-*d*) δ = 7.82 (d, J = 8.0 Hz, 2H), 7.46 – 7.37 (m, 3H), 4.64 – 4.54 (m, 1H), 3.09 – 3.00 (m, 2H), 2.97 – 2.87 (m, 1H), 2.58 – 2.45 (m, 3H), 2.40 – 2.32 (m, 1H), 1.67 – 1.61 (m, 2H), 1.60 – 1.53 (m, 1H), 0.93 (t, J = 7.4 Hz, 3H) ppm.

¹³C NMR (101 MHz, Chloroform-*d*) δ = 210.1, 173.0, 134.5, 130.7, 128.6 (2C), 127.8 (2C), 69.2, 49.6, 45.6, 35.3, 29.2, 17.4, 13.9 ppm.

HRMS (ESI) m/z calculated for C₁₅H₁₉NOH⁺ [M+H]⁺: 230.1539, found: 230.1541.

HPLC-Data: 66% *ee*, (Chiralpak AD-H column, $\lambda = 254$ nm, hexane/isopropanol = 95/5, flow rate = 0.5 mL/min): $t_R = 17.8$ (major), 23.1 (minor).

1-((2S)-4-Methyl-5-phenyl-3,4-dihydro-2H-pyrrol-2-yl)pentan-2-one (3ae)

The mixture of title compound was isolated through column chromatography (silica gel, petroleum ether/ethyl acetate = 5:1) as a colorless oil (17.4 mg, 36% yield, dr = 62:38). ¹H NMR (400 MHz, Chloroform-d) δ (mixture of two diastereomers) = 7.75 (d, J = 5.3 Hz, 1.2H), [7.65 (d, J = 4.9 Hz, 0.8H)], 7.42 – 7.29 (m, 3H), 4.54 – 4.41 (m, 1H), 3.46 – 3.35 (m, 1H), 3.09 – 2.97 (m, 1H), [2.62 – 2.54 (m, 0.4H)], 2.52 – 2.47 (m, 0.6H), 2.46 – 2.35 (m, 2H), 2.03 – 1.94 (m, 1H), 1.73 – 1.64 (m, 1H), 1.61 – 1.53 (m, 2H), [1.15 (d, J = 7.3 Hz, 1.2H)], 1.11 (d, J = 7.2 Hz, 1.8H), 0.86 (t, J = 7.0 Hz, 3H) ppm (peaks in brackets are for the minor diastereomer).

¹³C NMR (101 MHz, Chloroform-*d*) δ (mixture of two diastereomers) = 210.2, [210.0], 177.2, 133.5, 130.5, [130.2], 128.7 (2C), [128.5 (2C)], 128.2 (2C), [128.1 (2C)], [67.3], 66.7, [50.6], 49.8, 45.63, [45.56], [42.7], 42.2, 39.0, [38.2], [20.6], 18.3, 17.4, 13.9 ppm (peaks in brackets are for the minor diastereomer).

HRMS (ESI) m/z calculated for $C_{16}H_{21}NOH^{+}$ [M+H]⁺: 244.1696, found: 292.1699.

HPLC-Data: 40% *ee* (major diastereomer), 42% *ee* (minor diastereomer), (Chiral AD-H column, $\lambda = 254$ nm, hexane/isopropanol = 98/2, flow rate = 0.5 mL/min): $t_R = 29.3$ (major enantiomer, minor diastereomer), 33.4 (major enantiomer, major diastereomer), 39.0 (minor enantiomer, major diastereomer), 41.3 (minor enantiomer, minor diastereomer).

(S)-1-(2,4,4-Trimethyl-5-phenyl-3,4-dihydro-2H-pyrrol-2-yl)pentan-2-one (3af)

The title compound was isolated through column chromatography (silica gel, petroleum ether/ethyl acetate = 5:1) as a colorless oil (23.3 mg, 43% yield).

¹**H NMR** (400 MHz, Chloroform-*d*) δ = 7.65 (d, J = 7.8 Hz, 2H), 7.40 – 7.33 (m, 3H), 2.84 (d, J = 15.3 Hz, 1H), 2.72 (d, J = 15.3 Hz, 1H), 2.49 – 2.40 (m, 2H), 2.18 (d, J = 13.4 Hz, 1H), 1.94 (d, J = 13.4 Hz, 1H), 1.63 – 1.53 (m, 2H), 1.41 (s, 3H), 1.39 (s, 3H), 1.31 (s, 3H), 0.90 (t, J = 7.4 Hz, 3H) ppm.

¹³C NMR (101 MHz, Chloroform-*d*) δ = 210.3, 177.7, 135.1, 129.4, 128.3 (2C), 128.1 (2C), 70.8, 54.8, 51.8 (2C), 46.7, 29.2 (2C), 28.5, 17.3, 13.9 ppm.

HRMS (ESI) m/z calculated for C₁₈H₂₅NOH⁺ [M+H]⁺: 272.2009, found: 272.2011.

HPLC-Data: 54% *ee*, (Chiral AD-H column, $\lambda = 254$ nm, hexane/isopropanol = 95/5, flow rate = 0.5 mL/min): $t_R = 8.3$ (major), 8.9 (minor).

(S)-1-(4,4-Dimethyl-5-(p-tolyl)-3,4-dihydro-2H-pyrrol-2-yl)pentan-2-one (3ag)

The title compound was isolated through column chromatography (silica gel, petroleum ether/ethyl acetate = 4:1) as a colorless oil (34.7 mg, 64% yield).

¹**H NMR** (400 MHz, Chloroform-*d*) δ = 7.60 (d, J = 8.2 Hz, 2H), 7.17 (d, J = 7.9 Hz, 2H), 4.43 – 4.34 (m, 1H), 3.11 (dd, J = 16.3, 5.4 Hz, 1H), 2.53 (dd, J = 16.3, 8.6 Hz, 1H), 2.54 – 2.42 (m, 2H), 2.36 (s, 3H), 2.22 (dd, J = 12.6, 6.7 Hz, 1H), 1.69 – 1.59 (m, 2H), 1.48 (dd, J = 12.6, 8.7 Hz, 1H), 1.35 (s, 3H), 1.34 (s, 3H), 0.93 (t, J = 7.4 Hz, 3H) ppm.

¹³C NMR (101 MHz, Chloroform-*d*) δ = 210.2, 179.8, 139.8, 131.8, 129.0 (2C), 128.0 (2C), 64.0, 50.7, 49.9, 48.8, 45.7, 27.5, 26.0, 21.5, 17.3, 13.9 ppm.

HRMS (ESI) m/z calculated for C₁₈H₂₅NOH⁺ [M+H]⁺: 272.2009, found: 272.2010.

HPLC-Data: 98% *ee*, (Chiralpak AD-H column, $\lambda = 254$ nm, hexane/isopropanol = 90/10, flow rate = 0.5 mL/min): $t_R = 11.7$ (major), 12.3 (minor).

(S)-1-(5-(4-(*tert*-Butyl)phenyl)-4,4-dimethyl-3,4-dihydro-2*H*-pyrrol-2-yl)pentan-2-one (3ah)

The title compound was isolated through column chromatography (silica gel, petroleum ether/ethyl acetate = 6:1) as a colorless oil (35.2 mg, 56% yield).

¹**H NMR** (400 MHz, Chloroform-*d*) δ = 7.64 (d, J = 8.5 Hz, 2H), 7.37 (d, J = 8.5 Hz, 2H), 4.43 – 4.34 (m, 1H), 3.10 (dd, J = 16.2, 5.4 Hz, 1H), 2.52 (dd, J = 16.2, 8.7 Hz 1H), 2.53 – 2.42 (m, 2H), 2.22 (dd, J = 12.5, 6.8 Hz, 1H), 1.69 – 1.58 (m, 2H), 1.48 (dd, J = 12.6, 8.7 Hz, 1H), 1.36 (s, 3H), 1.35 (s, 3H), 1.31 (s, 9H), 0.93 (t, J = 7.4 Hz, 3H) ppm.

¹³C NMR (101 MHz, Chloroform-*d*) δ = 210.2, 179.6, 152.8, 131.7, 127.8 (2C), 125.2 (2C), 64.0, 50.6, 49.9, 48.7, 45.6, 34.8, 31.3 (3C), 27.6, 26.0, 17.3, 13.9 ppm.

HRMS (ESI) m/z calculated for $C_{21}H_{31}NONa^+$ [M+Na]⁺: 314.2478, found: 314.2484. **HPLC-Data**: 90% *ee*, (Chiral MD column, $\lambda = 254$ nm, hexane/isopropanol = 95/5, flow rate = 0.5 mL/min): $t_R = 9.2$ (major), 10.9 (minor).

(S)-1-(4,4-Dimethyl-5-(4-(trifluoromethoxy)phenyl)-3,4-dihydro-2*H*-pyrrol-2-yl)pentan-2-one (3ai)

The title compound was isolated through column chromatography (silica gel, petroleum ether/ethyl acetate = 4:1) as a colorless oil (49.8 mg, 73% yield).

¹H NMR (500 MHz, Chloroform-*d*) δ = 7.72 (d, J = 8.8 Hz, 2H), 7.20 (d, J = 8.8 Hz, 2H), 4.44 – 4.37 (m, 1H), 3.07 (dd, J = 16.5, 5.6 Hz, 1H), 2.54 (dd, J = 16.5, 8.5 Hz, 1H), 2.50 – 2.40 (m, 2H), 2.24 (dd, J = 12.6, 6.8 Hz, 1H), 1.67 – 1.59 (m, 2H), 1.50 (dd, J = 12.7, 8.9 Hz, 1H), 1.33 (s, 3H), 1.32 (s, 3H), 0.92 (t, J = 7.4 Hz, 3H) ppm. ¹³C NMR (126 MHz, Chloroform-*d*) δ = 209.8, 178.7, 150.2 (q, J = 1.9 Hz), 133.2, 129.7 (2C), 120.6 (2C), 120.5 (q, J = 257.7 Hz), 64.2, 50.7, 49.6, 48.6, 45.6, 27.3, 25.8,

¹⁹**F NMR** (471 MHz, Chloroform-*d*) $\delta = -57.76$ (s, 3F) ppm.

17.3, 13.8 ppm.

HRMS (ESI) m/z calculated for $C_{18}H_{22}F_3NO_2H^+$ [M+H]⁺: 342.1675, found: 342.1678. **HPLC-Data**: 90% *ee*, (Chiral MD column, $\lambda = 254$ nm, hexane/isopropanol = 90/10, flow rate = 0.5 mL/min): $t_R = 7.8$ (major), 8.5 (minor).

(S)-1-(5-(4-Fluorophenyl)-4,4-dimethyl-3,4-dihydro-2*H*-pyrrol-2-yl)pentan-2-one (3aj)

The title compound was isolated through column chromatography (silica gel, petroleum ether/ethyl acetate = 5:1) as a colorless oil (34.1 mg, 62% yield).

¹**H NMR** (400 MHz, Chloroform-*d*) δ = 7.72 – 7.65 (m, 2H), 7.08 – 7.00 (m, 2H), 4.43 – 4.34 (m, 1H), 3.08 (dd, J = 16.4, 5.5 Hz, 1H), 2.53 (dd, J = 16.5, 8.5 Hz, 1H), 2.50 – 2.40 (m, 2H), 2.23 (dd, J = 12.6, 6.8 Hz, 1H), 1.69 – 1.58 (m, 2H), 1.49 (dd, J = 12.6, 8.8 Hz, 1H), 1.34 (s, 3H), 1.32 (s, 3H), 0.93 (t, J = 7.4 Hz, 3H) ppm.

¹³C NMR (101 MHz, Chloroform-d) $\delta = 210.0, 178.9, 163.7$ (d, J = 249.5 Hz), 130.7

(d, J = 3.3 Hz), 130.0 (d, J = 8.3 Hz, 2C), 115.3 (d, J = 21.4 Hz, 2C), 64.0, 50.6, 49.7, 48.7, 45.6, 27.4, 25.9, 17.3, 13.9 ppm.

¹⁹**F NMR** (376 MHz, Chloroform-*d*) δ = –111.34 (s, 1F) ppm.

HRMS (ESI) m/z calculated for $C_{17}H_{22}FNONa^+$ [M+Na]⁺: 298.1578, found: 298.1582. **HPLC-Data**: 91% *ee*, (Chiral MD column, $\lambda = 254$ nm, hexane/isopropanol = 95/5, flow rate = 0.5 mL/min): $t_R = 9.7$ (minor), 10.7 (major).

(S)-1-(5-(4-Chlorophenyl)-4,4-dimethyl-3,4-dihydro-2*H*-pyrrol-2-yl)pentan-2-one (3ak)

The title compound was isolated through column chromatography (silica gel, petroleum ether/ethyl acetate = 5:1) as a yellow oil (38.4 mg, 66% yield).

¹H NMR (400 MHz, Chloroform-*d*) δ = 7.63 (d, J = 8.6 Hz, 2H), 7.33 (d, J = 8.6 Hz, 2H), 4.44 – 4.35 (m, 1H), 3.08 (dd, J = 16.4, 5.6 Hz, 1H), 2.53 (dd, J = 16.5, 8.5 Hz, 1H), 2.52 – 2.39 (m, 2H), 2.23 (dd, J = 12.6, 6.7 Hz, 1H), 1.68 – 1.58 (m, 2H), 1.49 (dd, J = 12.6, 8.8 Hz, 1H), 1.33 (s, 3H), 1.31 (s, 3H), 0.92 (t, J = 7.4 Hz, 3H) ppm. ¹³C NMR (101 MHz, Chloroform-*d*) δ = 209.9, 178.9, 135.8, 133.1, 129.4 (2C), 128.5 (2C), 64.2, 50.7, 49.7, 48.6, 45.6, 27.3, 25.9, 17.3, 13.9 ppm.

HRMS (ESI) m/z calculated for $C_{17}H_{22}ClNO_2H^+$ [M+H]⁺: 292.1463, found: 292.1466. **HPLC-Data**: 98% *ee*, (Chiral MD column, $\lambda = 254$ nm, hexane/isopropanol = 95/5, flow rate = 0.5 mL/min): $t_R = 10.0$ (minor), 11.2 (major).

(S)-2-(2-([1,1'-Biphenyl]-4-yl)-2-oxo-1-phenylethyl)cyclohex-2-en-1-one (3al)

The title compound was isolated through column chromatography (silica gel, petroleum ether/ethyl acetate = 5:1) as a yellow oil (32.4 mg, 50% yield).

¹**H NMR** (400 MHz, Chloroform-*d*) $\delta = 7.77$ (d, J = 8.1 Hz, 2H), 7.62 (d, J = 8.2 Hz, 2H), 4.48 – 4.40 (m, 1H), 3.09 (dd, J = 16.5, 5.6 Hz, 1H), 2.56 (dd, J = 16.6, 8.4 Hz,

1H), 2.52 - 2.42 (m, 2H), 2.26 (dd, J = 12.7, 6.8 Hz, 1H), 1.69 - 1.59 (m, 2H), 1.52 (dd, J = 12.6, 8.8 Hz, 1H), 1.35 (s, 3H), 1.32 (s, 3H), 0.93 (t, J = 7.4 Hz, 3H) ppm.

13C NMR (101 MHz, Chloroform-d) $\delta = 209.8$, 179.1, 138.2, 131.4 (q, J = 32.6 Hz), 128.4 (2C), 125.3 (q, J = 3.7 Hz, 2C), 124.1 (q, J = 272.2 Hz), 64.5, 50.9, 49.6, 48.5, 45.6, 27.2, 25.8, 17.3, 13.9 ppm.

¹⁹**F NMR** (376 MHz, Chloroform-*d*) δ = -62.81 (s, 3F) ppm.

HRMS (ESI) m/z calculated for $C_{18}H_{22}F_3NOH^+$ [M+H]⁺: 326.1726, found: 326.1736. **HPLC-Data**: 98% *ee*, (Chiral MD column, $\lambda = 254$ nm, hexane/isopropanol = 95/5, flow rate = 0.5 mL/min): $t_R = 9.7$ (major), 11.1 (minor).

tert-Butyl (S)-4-(4,4-dimethyl-2-(2-oxopentyl)-3,4-dihydro-2*H*-pyrrol-5-yl)-ben-zoate (3am)

$$tBuO_2C$$
 N
 O
 n -Pr
 N
 Me
 Me

The title compound was isolated through column chromatography (silica gel, petroleum ether/ethyl acetate = 4:1) as a white solid (50.8 mg, 71% yield).

¹**H NMR** (400 MHz, Chloroform-*d*) δ = 7.97 (d, J = 8.3 Hz, 2H), 7.69 (d, J = 8.3 Hz, 2H), 4.47 – 4.38 (m, 1H), 3.10 (dd, J = 16.5, 5.5 Hz, 1H), 2.55 (dd, J = 16.6, 8.5 Hz, 1H), 2.51 – 2.39 (m, 2H), 2.24 (dd, J = 12.6, 6.8 Hz, 1H), 1.68 – 1.60 (m, 2H), 1.58 (s, 9H), 1.49 (dd, J = 12.6, 8.9 Hz, 1H), 1.34 (s, 3H), 1.29 (s, 3H), 0.92 (t, J = 7.4 Hz, 3H) ppm.

¹³C NMR (101 MHz, Chloroform-*d*) δ = 209.9, 179.5, 165.4, 138.5, 132.8, 129.3 (2C), 127.8 (2C), 81.4, 64.4, 50.9, 49.6, 48.5, 45.6, 28.3 (3C), 27.2, 25.8, 17.3, 13.9 ppm.

HRMS (ESI) m/z calculated for $C_{22}H_{31}NO_3H^+$ [M+H]⁺: 358.2377, found: 358.2383.

HPLC-Data: 97% *ee*, (Chiral MD column, $\lambda = 254$ nm, hexane/isopropanol = 90/10, flow rate = 0.5 mL/min): $t_R = 8.3$ (major), 9.7 (minor).

(S)-1-(4,4-Dimethyl-5-(m-tolyl)-3,4-dihydro-2H-pyrrol-2-yl)pentan-2-one (3an)

The title compound was isolated through column chromatography (silica gel, petroleum ether/ethyl acetate = 5:1) as a colorless oil (33.3 mg, 61% yield).

¹**H NMR** (400 MHz, Chloroform-*d*) δ = 7.50 (s, 1H), 7.45 (d, J = 7.6 Hz, 1H), 7.25 (t, J = 6.9 Hz, 1H), 7.20 (d, J = 7.7 Hz, 1H), 4.45 – 4.36 (m, 1H), 3.13 (dd, J = 16.4, 5.3 Hz, 1H), 2.55 (dd, J = 16.4, 8.8 Hz, 1H), 2.53 – 2.43 (m, 2H), 2.37 (s, 3H), 2.24 (dd, J = 12.6, 6.7 Hz, 1H), 1.70 – 1.59 (m, 2H), 1.49 (dd, J = 12.6, 8.8 Hz, 1H), 1.35 (s, 3H), 1.33 (s, 3H), 0.94 (t, J = 7.4 Hz, 3H) ppm.

¹³C **NMR** (101 MHz, Chloroform-*d*) $\delta = 210.1$, 180.3, 138.0, 134.6, 130.4, 128.7, 128.1, 124.8, 64.0, 50.8, 49.8, 48.6, 45.6, 27.4, 26.0, 21.5, 17.3, 13.9 ppm.

HRMS (ESI) m/z calculated for $C_{18}H_{25}NONa^+$ [M+Na]⁺: 294.1828, found: 294.1829. **HPLC-Data**: 99% *ee*, (Chiral MD column, $\lambda = 254$ nm, hexane/isopropanol = 95/5, flow rate = 0.5 mL/min): $t_R = 12.1$ (minor), 12.9 (major).

(S)-1-(5-(3-Methoxyphenyl)-4,4-dimethyl-3,4-dihydro-2*H*-pyrrol-2-yl)pentan-2-one (3ao)

The title compound was isolated through column chromatography (silica gel, petroleum ether/ethyl acetate = 3:1) as a yellow oil (41.9 mg, 73% yield).

¹**H NMR** (400 MHz, Chloroform-*d*) δ = 7.31 – 7.22 (m, 3H), 6.97 – 6.92 (m, 1H), 4.45 – 4.36 (m, 1H), 3.83 (s, 3H), 3.12 (dd, J = 16.4, 5.4 Hz, 1H), 2.55 (dd, J = 16.4, 8.6 Hz, 1H), 2.52 – 2.41 (m, 2H), 2.24 (dd, J = 12.6, 6.7 Hz, 1H), 1.70 – 1.60 (m, 2H), 1.50 (dd, J = 12.6, 8.7 Hz, 1H), 1.35 (s, 3H), 1.34 (s, 3H), 0.94 (t, J = 7.4 Hz, 3H) ppm.

¹³C **NMR** (101 MHz, Chloroform-*d*) $\delta = 210.1$, 179.9, 159.5, 136.1, 129.3, 120.4, 115.5, 113.4, 64.1, 55.4, 50.8, 49.8, 48.6, 45.7, 27.5, 26.0, 17.3, 13.9 ppm.

HRMS (ESI) m/z calculated for $C_{18}H_{25}NO_2H^+$ [M+H]⁺: 288.1958, found: 288.1964. **HPLC-Data**: 96% *ee*, (Chiralpak IA column, $\lambda = 254$ nm, hexane/isopropanol = 95/5, flow rate = 0.5 mL/min): $t_R = 16.0$ (major), 16.9 (minor).

(S)-1-(5-(3-Fluorophenyl)-4,4-dimethyl-3,4-dihydro-2*H*-pyrrol-2-yl)pentan-2-one (3ap)

The title compound was isolated through column chromatography (silica gel, petroleum ether/ethyl acetate = 5:1) as a colorless oil (39.5 mg, 72% yield).

¹**H NMR** (400 MHz, Chloroform-*d*) δ = 7.44 (d, J = 7.7 Hz, 1H), 7.38 (d, J = 10.1 Hz, 1H), 7.36 – 7.29 (m, 1H), 7.08 (t, J = 8.4 Hz, 1H), 4.45 – 4.36 (m, 1H), 3.08 (dd, J = 16.4, 5.6 Hz, 1H), 2.53 (dd, J = 16.5, 8.5 Hz, 1H), 2.52 – 2.39 (m, 2H), 2.24 (dd, J = 12.6, 6.8 Hz, 1H), 1.69 – 1.58 (m, 2H), 1.50 (dd, J = 12.6, 8.9 Hz, 1H), 1.34 (s, 3H), 1.32 (s, 3H), 0.93 (t, J = 7.4 Hz, 3H) ppm.

¹³C NMR (101 MHz, Chloroform-*d*) $\delta = 209.9$, 178.9 (d, J = 2.4 Hz), 162.6 (d, J = 246.0 Hz), 136.8 (d, J = 7.4 Hz), 129.9 (d, J = 8.1 Hz), 123.7 (d, J = 3.0 Hz), 116.6 (d, J = 21.2 Hz), 115.1 (d, J = 22.5 Hz), 64.2, 50.8, 49.7, 48.6, 45.6, 27.3, 25.9, 17.3, 13.9 ppm.

¹⁹**F NMR** (376 MHz, Chloroform-*d*) δ = –112.83 (s, 1F) ppm.

HRMS (ESI) m/z calculated for $C_{17}H_{22}FNONa^+$ [M+Na]⁺: 298.1578, found: 298.1581. **HPLC-Data**: 98% *ee*, (Chiral MD column, $\lambda = 254$ nm, hexane/isopropanol = 95/5, flow rate = 0.5 mL/min): $t_R = 10.6$ (minor), 11.1 (major).

(S)-1-(5-(3-Chlorophenyl)-4,4-dimethyl-3,4-dihydro-2*H*-pyrrol-2-yl)pentan-2-one (3aq)

The title compound was isolated through column chromatography (silica gel, petroleum ether/ethyl acetate = 5:1) as a yellow oil (40.9 mg, 70% yield).

¹**H NMR** (400 MHz, Chloroform-*d*) δ = 7.66 (s, 1H), 7.53 (d, J = 7.7 Hz, 1H), 7.36 (d, J = 8.3 Hz, 1H), 7.29 (t, J = 7.8 Hz, 1H), 4.46 – 4.36 (m, 1H), 3.08 (dd, J = 16.5, 5.5 Hz, 1H), 2.53 (dd, J = 16.6, 8.5 Hz, 1H), 2.52 – 2.41 (m, 2H), 2.23 (dd, J = 12.6, 6.8 Hz, 1H), 1.68 – 1.58 (m, 2H), 1.49 (dd, J = 12.6, 8.9 Hz, 1H), 1.33 (s, 3H), 1.31 (s, 3H), 0.93 (t, J = 7.4 Hz, 3H) ppm.

¹³C **NMR** (101 MHz, Chloroform-*d*) $\delta = 209.8$, 178.9, 136.5, 134.3, 129.7, 129.6, 128.2, 126.0, 64.2, 50.8, 49.6, 48.5, 45.6, 27.3, 25.9, 17.3, 13.9 ppm.

HRMS (ESI) m/z calculated for $C_{17}H_{22}CINOH^+$ [M+H]⁺: 292.1463, found: 292.1467. **HPLC-Data**: 97% *ee*, (Chiral MD column, $\lambda = 254$ nm, hexane/isopropanol = 95/5, flow rate = 0.5 mL/min): $t_R = 10.6$ (major), 12.0 (minor).

(S)-1-(5-(3-Bromophenyl)-4,4-dimethyl-3,4-dihydro-2*H*-pyrrol-2-yl)pentan-2-one (3ar)

The title compound was isolated through column chromatography (silica gel, petroleum ether/ethyl acetate = 5:1) as a yellow oil (44.5 mg, 66% yield).

¹**H NMR** (400 MHz, Chloroform-*d*) δ = 7.82 (s, 1H), 7.57 (d, J = 7.8 Hz, 1H), 7.51 (d, J = 8.1 Hz, 1H), 7.23 (t, J = 7.9 Hz, 1H), 4.46 – 4.36 (m, 1H), 3.09 (dd, J = 16.6, 5.5 Hz, 1H), 2.53 (dd, J = 16.6, 8.5 Hz, 1H), 2.52 – 2.39 (m, 2H), 2.23 (dd, J = 12.6, 6.8 Hz, 1H), 1.68 – 1.58 (m, 2H), 1.49 (dd, J = 12.6, 8.8 Hz, 1H), 1.33 (s, 3H), 1.31 (s, 3H), 0.93 (t, J = 7.4 Hz, 3H) ppm.

¹³C **NMR** (101 MHz, Chloroform-*d*) $\delta = 209.8$, 178.8, 136.7, 132.6, 131.1, 129.8, 126.4, 122.5, 64.2, 50.8, 49.6, 48.5, 45.6, 27.3, 25.8, 17.3, 13.9 ppm.

HRMS (ESI) m/z calculated for $C_{17}H_{22}BrNOH^+$ [M+H]⁺: 336.0958, found: 336.0962. **HPLC-Data**: 96% *ee*, (Chiral MD column, $\lambda = 254$ nm, hexane/isopropanol = 90/10, flow rate = 0.5 mL/min): $t_R = 8.8$ (major), 10.0 (minor).

(S)-1-(4,4-Dimethyl-5-(3-(trifluoromethyl)phenyl)-3,4-dihydro-2*H*-pyrrol-2-yl)-pentan-2-one (3as)

The title compound was isolated through column chromatography (silica gel, petroleum ether/ethyl acetate = 5:1) as a yellow oil (43.4 mg, 67% yield).

¹**H NMR** (400 MHz, Chloroform-*d*) δ = 7.95 (s, 1H), 7.85 (d, J = 7.8 Hz, 1H), 7.64 (d, J = 7.8 Hz, 1H), 7.49 (t, J = 7.8 Hz, 1H), 4.48 – 4.39 (m, 1H), 3.10 (dd, J = 16.5, 5.6 Hz, 1H), 2.55 (dd, J = 16.5, 8.3 Hz, 1H), 2.51 – 2.40 (m, 2H), 2.26 (dd, J = 12.6, 6.8 Hz, 1H), 1.69 – 1.59 (m, 2H), 1.52 (dd, J = 12.7, 8.8 Hz, 1H), 1.35 (s, 3H), 1.33 (s, 3H), 0.93 (t, J = 7.4 Hz, 3H) ppm.

¹³C NMR (101 MHz, Chloroform-*d*) δ = 209.8, 178.7, 135.5, 131.1, 130.8 (q, *J* = 32.5 Hz), 128.8, 126.3 (q, *J* = 3.7 Hz), 124.1 (q, *J* = 273.2 Hz), 124.9 (q, *J* = 3.8 Hz), 64.4, 50.8, 49.6, 48.6, 45.6, 27.3, 25.8, 17.3, 13.8 ppm.

¹⁹**F NMR** (376 MHz, Chloroform-*d*) δ = –62.71 (s, 3F) ppm.

HRMS (ESI) m/z calculated for $C_{18}H_{22}F_3NOH^+$ [M+H]⁺: 326.1726, found: 326.1727. **HPLC-Data**: 98% *ee*, (Chiral MD column, $\lambda = 254$ nm, hexane/isopropanol = 90/10, flow rate = 0.5 mL/min): $t_R = 7.8$ (major), 8.4 (minor).

(S)-1-(5-(2-Fluorophenyl)-4,4-dimethyl-3,4-dihydro-2*H*-pyrrol-2-yl)pentan-2-one (3at)

The title compound was isolated through column chromatography (silica gel, petroleum ether/ethyl acetate = 5:1) as a colorless oil (33.5 mg, 61% yield).

¹**H NMR** (400 MHz, Chloroform-*d*) δ = 7.38 – 7.31 (m, 1H), 7.25 (t, *J* = 7.4 Hz, 1H), 7.14 (t, *J* = 7.5 Hz, 1H), 7.09 (t, *J* = 9.1 Hz, 1H), 4.55 – 4.45 (m, 1H), 3.13 (dd, *J* = 16.7, 5.3 Hz, 1H), 2.59 (dd, *J* = 16.7, 8.6 Hz, 1H), 2.52 – 2.40 (m, 2H), 2.26 (dd, *J* = 16.7, 8.6 Hz, 1H), 2.26 (dd, *J* = 16.7

12.6, 6.9 Hz, 1H), 1.68 - 1.58 (m, 2H), 1.51 (dd, J = 12.7, 8.6 Hz, 1H), 1.19 (s, 3H), 1.16 (s, 3H), 0.92 (t, J = 7.4 Hz, 3H) ppm.

¹³C NMR (101 MHz, Chloroform-*d*) δ = 209.8, 178.9, 159.8 (d, *J* = 247.8 Hz), 130.6 (d, *J* = 8.1 Hz), 130.3 (d, *J* = 3.6 Hz), 123.9 (d, *J* = 3.6 Hz), 123.4 (d, *J* = 17.0 Hz), 116.0 (d, *J* = 22.3 Hz), 65.4, 52.3, 49.6, 46.6, 45.6, 26.4 (d, *J* = 2.6 Hz), 25.0 (d, *J* = 2.7 Hz), 17.3, 13.9 ppm.

¹⁹**F NMR** (376 MHz, Chloroform-*d*) δ = –112.49 (s, 1F) ppm.

HRMS (ESI) m/z calculated for $C_{17}H_{22}FNOH^+$ [M+H]⁺: 276.1758, found: 276.1765. **HPLC-Data**: 95% *ee*, (Chiral MD column, $\lambda = 254$ nm, hexane/isopropanol = 95/5, flow rate = 0.5 mL/min): $t_R = 14.1$ (minor), 15.2 (major).

(S)-1-(4,4-Dimethyl-5-(naphthalen-2-yl)-3,4-dihydro-2*H*-pyrrol-2-yl)pentan-2-one (3au)

The title compound was isolated through column chromatography (silica gel, petroleum ether/ethyl acetate = 5:1) as a colorless oil (28.9 mg, 47% yield).

¹H NMR (400 MHz, Chloroform-*d*) δ = 8.15 (s, 1H), 7.90 – 7.80 (m, 4H), 7.54 – 7.46 (m, 2H), 4.52 – 4.42 (m, 1H), 3.17 (dd, J = 16.4, 5.4 Hz, 1H), 2.59 (dd, J = 16.5, 8.7 Hz, 1H), 2.55 – 2.43 (m, 2H), 2.29 (dd, J = 12.6, 6.7 Hz, 1H), 1.71 – 1.61 (m, 2H), 1.56 (dd, J = 12.6, 8.8 Hz, 1H), 1.45 (s, 3H), 1.43 (s, 3H), 0.95 (t, J = 7.4 Hz, 3H) ppm. ¹³C NMR (101 MHz, Chloroform-*d*) δ = 210.1, 179.8, 133.9, 132.9, 132.1, 128.8, 128.0, 127.8, 127.7, 127.0, 126.4, 125.7, 64.3, 50.9, 49.9, 48.9, 45.7, 27.7, 26.2, 17.4,

HRMS (ESI) m/z calculated for $C_{21}H_{25}NOH^+$ [M+H]⁺: 308.2009, found: 308.2013. **HPLC-Data**: 98% *ee*, (Chiral MD column, $\lambda = 254$ nm, hexane/isopropanol = 95/5, flow rate = 0.5 mL/min): $t_R = 15.8$ (major), 20.6 (minor).

13.9 ppm.

(S)-1-(4,4-Dimethyl-5-(thiophen-3-yl)-3,4-dihydro-2*H*-pyrrol-2-yl)pentan-2-one (3av)

The title compound was isolated through column chromatography (silica gel, petroleum ether/ethyl acetate = 4:1) as a yellow oil (22.3 mg, 42% yield).

¹**H NMR** (400 MHz, Chloroform-*d*) δ = 7.71 (s, 1H), 7.51 (d, J = 5.1 Hz, 1H), 7.32 – 7.28 (m, 1H), 4.43 – 4.34 (m, 1H), 3.09 (dd, J = 16.3, 5.4 Hz, 1H), 2.52 (dd, J = 16.3, 8.7 Hz 1H), 2.51 – 2.40 (m, 2H), 2.23 (dd, J = 12.7, 7.0 Hz, 1H), 1.69 – 1.59 (m, 2H), 1.47 (dd, J = 12.7, 8.5 Hz, 1H), 1.40 (s, 3H), 1.34 (s, 3H), 0.93 (t, J = 7.4 Hz, 3H) ppm. ¹³**C NMR** (101 MHz, Chloroform-*d*) δ = 210.1, 175.1, 135.9, 128.2, 126.1, 125.4, 64.4, 50.5, 50.0, 48.1, 45.6, 27.8, 26.1, 17.4, 13.9 ppm.

HRMS (ESI) m/z calculated for $C_{15}H_{21}NOSNa^+$ [M+Na]⁺: 286.1236, found: 286.1245. **HPLC-Data**: 90% *ee*, (Chiral AD-H column, $\lambda = 254$ nm, hexane/isopropanol = 95/5, flow rate = 0.5 mL/min): $t_R = 18.3$ (major), 21.8 (minor).

Synthesis of Compound 3aa on a 2.0 mmol Scale

Tetrabutyl ammonium decatungstate (TBADT) (332.0 mg, 0.1 mmol, 5 mol%), Ni(ClO₄)₂·6H₂O (109.7 mg, 0.3 mmol, 15 mol%), the ligand **L1** (128.3 mg, 0.36 mmol, 18 mol%), NaClO₄ (122.4 mg, 1.0 mmol, 0.5 equiv), and the oxime ester **2a** (698.4 mg, 2.0 mmol, 1 equiv) were placed in an oven-dried Schlenk tube equipped with a magnetic stirring bar. The tube was evacuated and filled with nitrogen (three cycles). To these solids, dry MeCN (10 mL, 0.2 M) and butanal (**1a**, 0.55 mL, 6.0 mmol, 3 equiv) were sequentially added under nitrogen atmosphere. Subsequently, the reaction mixture was stirred and irradiated using two 34 W 390 nm LED lamps (Kessil PR160-390, 5 cm away, with adequate fans keep the reaction at room temperature) for 24 h. After exposing to air for 15 minutes, the reaction mixture was filtered through a pad of Celite and concentrated under reduced pressure. The residue was purified through column chromatography (silica gel, EtOAc/petroleum ether = 1:5) to afford the desired product **3aa** (329.0 mg, 1.28 mmol, 64% yield, 98% *ee*).

Derivatizations of the Imino-acylation Products 3aa and 3ha

An oven-dried test tube was charged with methyl triphenylphosphonium bromide (107 mg, 0.3 mmol, 3 equiv), to which dry THF (1 mL) was added under N₂ atmosphere. The resulting suspension was cooled to 0 °C, and *n*-BuLi (0.1 mL, 0.25 mmol, 2.5 equiv, 2.5 M solution in hexane) was added. After the resulting yellow solution was stirred for 30 minutes, a solution of **3aa** (98% *ee*, 25.7 mg, 0.1 mmol, 1 equiv) in THF (0.5 mL) was added to the reaction mixture. The cooling bath was then removed, and the solution was stirred at room temperature. After 16 h, the reaction was quenched with sat. aq. NH₄Cl solution. The organic layer was separated, and the aqueous layer was extracted with Et₂O. The combined organic layers were concentrated under reduced pressure. The residue was purified through column chromatography on silica gel (EtOAc/petroleum ether = 1:9) to give (*R*)-4,4-dimethyl-2-(2-methylenepentyl)-5-phenyl-3,4-dihydro-2H-pyrrole (4) as a colorless oil in 61% yield (15.5 mg) and 98% *ee*.

¹**H NMR** (400 MHz, Chloroform-*d*) δ = 7.69 (d, J = 7.7 Hz, 2H), 7.41 – 7.34 (m, 3H), 4.82 (s, 2H), 4.22 – 4.13 (m, 1H), 2.81 (dd, J = 14.1, 5.0 Hz, 1H), 2.11 – 2.02 (m, 4H), 1.57 (dd, J = 12.6, 8.5 Hz 1H), 1.56 – 1.47 (m, 2H), 1.35 (s, 6H), 0.93 (t, J = 7.3 Hz, 3H) ppm.

¹³C NMR (101 MHz, Chloroform-*d*) δ = 179.3, 147.5, 135.1, 129.5, 128.3 (2C), 128.0 (2C), 111.0, 66.8, 50.5, 48.0, 43.6, 38.6, 27.6, 26.3, 21.0, 14.0 ppm.

HRMS (ESI) m/z calculated for $C_{18}H_{25}NH^{+}$ [M+H]⁺: 256.2060, found: 256.2072.

HPLC-Data: 98% *ee*, (Chiral AD-H column, $\lambda = 254$ nm, hexane/isopropanol = 98/2, flow rate = 0.5 mL/min): $t_R = 8.0$ (major), 9.5 (minor).

A solution of TsNHNH₂ (41.0 mg, 0.22 mmol, 1.1 equiv) in MeOH (1 mL) was stirred at 60 °C until TsNHNH₂ was completely dissolved. Subsequently, compound **3aa** (98% *ee*, 51.4 mg, 0.2 mmol, 1 equiv) was slowly added to the mixture. After stirring at 60°C for 12 h, the reaction mixture was cooled to room temperature and quenched with H₂O. The organic layer was separated, and the aqueous layer was extracted with EtOAc. The combined organic layers were concentrated under reduced pressure. The residue was purified through column chromatography on silica gel (EtOAc/petroleum ether = 1:5) to give (S,Z)-N'-(1-(4,4-dimethyl-5-phenyl-3,4-dihydro-2H-pyrrol-2-yl)pentan-2-ylidene)-4-methylbenzenesulfonohydrazide (**5**) as a white solid in 53% yield (44.9 mg) and 96% *ee*.

¹**H NMR** (400 MHz, Chloroform-*d*) δ = 11.44 – 11.18 (brs, 1H), 7.83 (d, J = 6.4 Hz, 2H), 7.72 (d, J = 8.2 Hz, 2H), 7.52 – 7.43 (m, 3H), 7.14 (d, J = 8.0 Hz, 2H), 3.91 – 3.79 (m, 1H), 2.61 (dd, J = 13.3, 11.4 Hz, 1H), 2.33 (s, 3H), 2.28 – 2.20 (m, 3H), 2.06 (dd, J = 12.3, 6.1 Hz, 1H), 1.60 (dd, J = 12.5, 10.4 Hz, 1H), 1.58 – 1.49 (m, 2H), 1.37 (s, 3H), 1.34 (s, 3H), 0.83 (t, J = 7.4 Hz, 3H) ppm.

¹³C NMR (101 MHz, Chloroform-*d*) δ = 181.5, 160.1, 142.9, 136.6, 133.2, 130.6, 129.2 (2C), 128.5 (2C), 128.2 (2C), 128.0 (2C), 66.5, 50.1, 49.3, 40.5, 37.6, 26.9, 24.9, 21.6, 19.4, 13.8 ppm.

HRMS (ESI) m/z calculated for $C_{24}H_{31}N_3O_2SH^+$ [M+H]⁺: 426.2210, found: 426.2211. **HPLC-Data**: 96% *ee*, (Chiral MD column, $\lambda = 254$ nm, hexane/isopropanol = 90/10, flow rate = 0.5 mL/min): $t_R = 17.5$ (minor), 26.4 (major).

A solution of **3aa** (98% *ee*, 25.7 mg, 0.1 mmol, 1 equiv), *m*-CPBA (34.5 mg, 0.2 mmol, 2 equiv) and NaHCO₃ (16.8 mg, 0.2 mmol, 2 equiv) in DCM (1 mL) were stirred at room temperature for 12 h. The resulting mixture was concentrated under reduced pressure. The residue was purified through column chromatography on silica gel (EtOAc/petroleum ether = 1:6) to give *1-((2S,5S)-4,4-dimethyl-5-phenyl-6-oxa-1-azabicyclo[3.1.0]hexan-2-yl)pentan-2-one* (6) as a colorless oil in 68% yield (18.6 mg, >98:2 dr) and 98% *ee*.

¹**H NMR** (400 MHz, Chloroform-*d*) δ = 7.41 – 7.31 (m, 5H), 3.98 – 3.88 (m, 1H), 3.10 (dd, J = 17.1, 5.7 Hz, 1H), 2.61 (dd, J = 17.1, 7.5 Hz, 1H), 2.52 – 2.41 (m, 2H), 1.79 (dd, J = 12.3, 6.9 Hz, 1H), 1.67 – 1.58 (m, 2H), 1.32 (dd, J = 12.4, 9.9 Hz, 1H), 1.26 (s, 3H), 1.02 (s, 3H), 0.92 (t, J = 7.4 Hz, 3H) ppm.

¹³C NMR (101 MHz, Chloroform-*d*) δ = 209.3, 133.7, 128.8, 128.0 (2C), 127.6 (2C), 94.2, 60.9, 45.8, 45.6, 42.6, 41.3, 24.4, 22.7, 17.3, 13.8 ppm.

HRMS (ESI) m/z calculated for $C_{17}H_{23}NO_2H^+$ [M+H]⁺: 274.1802, found: 274.1811.

HPLC-Data: 98% *ee*, (Chiral MD column, $\lambda = 190$ nm, hexane/isopropanol = 90/10, flow rate = 0.5 mL/min): $t_R = 23.0$ (minor), 30.1 (major).

An oven-dried test tube was charged with **3aa** (98% *ee*, 25.7 mg, 0.1 mmol, 1 equiv), to which dry DCM (1 mL) was added under N₂ atmosphere. DIBAL-H (0.3 mL, 0.3 mmol, 3 equiv, 1.0 M solution in hexane) was added dropwise to the reaction mixture at –78 °C. After stirring for 5 h, the reaction was quenched with 1N HCl. The organic layer was separated and the aqueous layer was extracted with DCM. The combined organic layers were concentrated under reduced pressure. The residue was purified through column chromatography on silica gel (EtOAc/petroleum ether = 1:3) to give *I*-((S)-4,4-dimethyl-5-phenyl-3,4-dihydro-2H-pyrrol-2-yl)pentan-2-ol (7) as a colorless oil in 54% yield (14.1 mg, >98:2 dr) and 98% *ee*.

¹**H NMR** (500 MHz, Chloroform-*d*) δ = 7.71 (d, J = 7.9 Hz, 2H), 7.44 – 7.33 (m, 3H), 4.50 – 4.07 (brs, 1H), 4.32 – 4.23 (m, 1H), 3.98 – 3.90 (m, 1H), 2.09 (dd, J = 12.4, 6.6 Hz, 1H), 1.95 – 1.88 (m, 1H), 1.80 – 1.73 (m, 1H), 1.71 – 1.64 (m, 1H), 1.60 (dd, J = 12.4, 9.4 Hz, 1H), 1.56 – 1.49 (m, 2H), 1.39 (s, 3H), 1.36 (s, 3H), 1.29 – 1.24 (m, 1H), 0.96 (t, J = 7.1 Hz, 3H) ppm.

¹³C NMR (126 MHz, Chloroform-*d*) δ = 179.6, 134.2, 129.9, 128.4 (2C), 128.0 (2C), 70.2, 64.6, 49.7, 49.1, 42.2, 39.3, 27.3, 25.8, 19.5, 14.4 ppm.

HRMS (ESI) m/z calculated for C₁₇H₂₅NOH⁺ [M+H]⁺: 260.2009, found: 260.2009.

HPLC-Data: 98% *ee*, (Chiral MD column, $\lambda = 254$ nm, hexane/isopropanol = 95/5, flow rate = 0.5 mL/min): $t_R = 10.0$ (minor), 11.3 (major).

Ph
$$\stackrel{\text{N}}{\longrightarrow} 0$$
 $\stackrel{\text{n-Pr}}{\longrightarrow} 0$ $\stackrel{\text{N}}{\longrightarrow} 0$

An oven-dried test tube was charged with **3aa** (98% *ee*, 25.7 mg, 0.1 mmol, 1 equiv), to which dry THF (1 mL) was added under N₂ atmosphere. *n*-PrMgBr (0.3 mL, 0.3 mmol, 3 equiv, 1.0 M solution in THF) was added dropwise to the reaction mixture at 0 °C. After the resulting yellow solution was stirred for 10 min, the cooling bath was then removed, and the reaction mixture was stirred at room temperature. After 12 h, the reaction was quenched with sat. aq. NH₄Cl solution. The organic layer was separated, and the aqueous layer was extracted with Et₂O. The combined organic layers were concentrated under reduced pressure. The residue was purified through column chromatography on silica gel (EtOAc/petroleum ether = 1:9) to give (*S*)-4-((4,4-dimethyl-5-phenyl-3,4-dihydro-2H-pyrrol-2-yl)methyl)heptan-4-ol (**8**) as a colorless oil in 88% yield (26.5 mg) and 96% *ee*.

¹**H NMR** (400 MHz, Chloroform-*d*) δ = 7.73 (d, J = 7.9 Hz, 2H), 7.44 – 7.31 (m, 3H), 6.20 – 5.46 (brs, 1H), 4.30 – 4.19 (m, 1H), 2.10 (dd, J = 12.4, 6.5 Hz, 1H), 1.88 (dd, J = 14.1, 3.7 Hz, 1H), 1.77 – 1.61 (m, 2H), 1.59 – 1.49 (m, 2H), 1.42 (s, 3H), 1.48 – 1.24 (m, 6H), 1.36 (s, 3H), 0.95 (t, J = 7.4 Hz, 3H), 0.91 (t, J = 7.4 Hz, 3H) ppm.

¹³C NMR (101 MHz, Chloroform-*d*) $\delta = 178.8$, 133.8, 130.1, 128.3 (2C), 128.1 (2C), 74.4, 64.3, 49.9, 49.1, 45.8, 42.8, 41.1, 27.3, 26.0, 17.9, 16.7, 15.02, 14.96 ppm.

HRMS (ESI) m/z calculated for C₂₀H₃₁NOH⁺ [M+H]⁺: 302.2478, found: 302.2080.

HPLC-Data: 96% *ee*, (Chiral MD column, $\lambda = 254$ nm, hexane/isopropanol = 95/5, flow rate = 0.5 mL/min): $t_R = 8.0$ (minor), 15.8 (major).

An oven-dried test tube was charged with **3ha** (92% ee, 145.5 mg, 0.5 mmol, 1 equiv), to which dry THF (2 mL) was added under N₂ atmosphere. PhMgBr (1.5 mL, 1.5 mmol, 3 equiv, 1.0 M solution in THF) was added dropwise to the reaction mixture at 0 °C. After the resulting yellow solution was stirred for 10 min, the cooling bath was removed, and the reaction mixture was stirred at room temperature for 12 h. Subsequently, the reaction was quenched with sat. aq. NH₄Cl solution. The organic layer was separated, and the aqueous layer was extracted with Et₂O. The combined organic layers were concentrated under reduced pressure. The residue was purified through column chromatography on silica gel (EtOAc/petroleum ether = 1:9) to give (S)-2-(4,4-dimethyl-5-phenyl-3,4-dihydro-2H-pyrrol-2-yl)-1,1-diphenylethan-1-ol (9) as a white solid in 60% yield (110.8 mg) and 90% ee.

¹**H NMR** (500 MHz, Chloroform-*d*) δ = 7.79 (d, J = 8.5 Hz, 2H), 7.76 – 7.57 (brs, 1H), 7.64 (d, J = 8.2 Hz, 2H), 7.54 (d, J = 8.3 Hz, 2H), 7.44 – 7.30 (m, 7H), 7.26 – 7.18 (m, 2H), 4.04 – 3.95 (m, 1H), 2.90 (dd, J = 14.0, 3.0 Hz, 1H), 2.23 (dd, J = 14.0, 11.7 Hz, 1H), 2.11 (dd, J = 12.4, 6.6 Hz, 1H), 1.65 (dd, J = 12.4, 9.2 Hz, 1H), 1.38 (s, 3H), 1.32 (s, 3H) ppm.

¹³C **NMR** (126 MHz, Chloroform-*d*) δ = 178.7, 148.7, 147.5, 133.6, 130.2, 128.4 (2C), 128.18 (4C), 128.16 (2C), 126.6, 126.5 (2C), 126.4, 125.8 (2C), 78.5, 64.9, 49.4, 49.0, 47.7, 27.3, 25.9 ppm.

HRMS (ESI) m/z calculated for $C_{26}H_{27}NOH^{+}$ [M+H]⁺: 370.2165, found: 370.2170.

HPLC-Data: 90% *ee*, (Chiral MD column, $\lambda = 254$ nm, hexane/isopropanol = 95/5, flow rate = 0.5 mL/min): $t_R = 11.0$ (minor), 14.0 (major).

A solution of **9** (90% *ee*, 110.8 mg, 0.3 mmol, 1 equiv), NaBH(OAc)₃ (127.1 mg, 0.6 mmol, 2 equiv) and HOAc (35 μL, 0.6 mmol, 2 equiv) in 1,2-DCE (1.5 mL) were stirred at room temperature for 12 h. Next, the mixture was concentrated under reduced pressure and the residue was purified through column chromatography on silica gel (EtOAc/petroleum ether = 1:2) to give *2-((2S,5S)-4,4-dimethyl-5-phenylpyrrolidin-2-yl)-1,1-diphenylethan-1-ol* (**10**) as a white solid in 75% yield (83.0 mg, 10:1 dr) and 92% *ee*.

¹H NMR (500 MHz, Chloroform-*d*) δ (mixture of two diastereomers) = 7.56 (d, J = 8.4 Hz, 2H), [7.48 (d, J = 7.9 Hz, 0.18H)], 7.44 (d, J = 8.2 Hz, 1.82H), 7.38 – 7.23 (m, 8H), 7.21 – 7.07 (m, 3H), 3.84 (s, 0.91H), [3.81 (s, 0.09H)], 3.53 – 3.44 (m, 0.91H), [3.44 – 3.39 (m, 0.09H)], [2.74 (dd, J = 14.2, 4.2 Hz, 0.09H)], 2.56 (dd, J = 14.3, 3.1 Hz, 0.91H), [2.46 (dd, J = 14.2, 11.0 Hz, 0.09H)], 2.24 (dd, J = 14.3, 11.6 Hz, 0.91H), 2.00 (dd, J = 12.8, 8.0 Hz, 1H), [1.57 (dd, J = 12.8, 4.6 Hz, 0.09H)], 1.49 (dd, J = 12.9, 7.4 Hz, 0.91H), 1.05 (s, 2.73H), [0.99 (s, 0.27H)], [0.77 (s, 0.27H)], 0.53 (s, 2.73H) ppm (peaks in brackets are for the minor diastereomer).

¹³C NMR (126 MHz, Chloroform-*d*) δ (mixture of two diastereomers) = 149.0, [148.4], 147.6, [147.1], [139.8], 137.4, [128.4], 128.3 (2C), [128.2], 128.13 (2C), 128.11 (2C), [128.05 (2C)], [127.7], 127.4, [127.3], 127.1 (2C), [126.7], 126.55, 126.48 (2C), 126.35, [126.27], [125.7], [125.61], 125.60 (2C), [78.7], 78.2, [72.6], 70.1, 52.7, [52.3], 49.4, [47.5], [46.8], 46.2, 43.2, [41.6], [27.6], 26.2, [24.2], 22.3 ppm (peaks in brackets are for the minor diastereomer).

HRMS (ESI) m/z calculated for $C_{26}H_{29}NOH^{+}$ [M+H]⁺: 372.2322, found: 372.2333.

HPLC-Data: 92% ee, (Chiralpak AD-H column, $\lambda = 254$ nm, hexane/isopropanol =

65/35, flow rate = 0.5 mL/min): $t_R = 8.0$ (minor enantiomer, major diastereomer), 9.6 (major enantiomer, minor diastereomer), 10.7 (major enantiomer, major diastereomer), 11.5 (minor enantiomer, minor diastereomer).

Mechanistic Studies

Control Experiments

Tetrabutyl ammonium decatungstate (TBADT) (33.2 mg, 0.01 mmol, 5 mol%), Ni(ClO₄)₂·6H₂O (11.0 mg, 0.03 mmol, 15 mol%), the ligand L1 (12.8 mg, 0.036 mmol, 18 mol%), NaClO₄ (12.2 mg, 0.1 mmol, 0.5 equiv), and the oxime ester 2a-1 or 2a-2 (0.2 mmol, 1 equiv) were placed in an oven-dried test tube equipped with a magnetic stirring bar. The tube was evacuated and filled with nitrogen (three cycles). To these solids, dry MeCN (1 mL, 0.2 M) and butanal (1a, 55 μL, 0.6 mmol, 3 equiv) were sequentially added under nitrogen atmosphere. Subsequently, the reaction mixture was stirred and irradiated using two 34 W 390 nm LED lamps (Kessil PR160-390, 5 cm away, with adequate fans keep the reaction at room temperature) for 24 h. After exposing to air for 15 minutes, the reaction mixture was filtered through a pad of Celite and concentrated under reduced pressure. The residue was purified through column chromatography on silica gel (EtOAc/petroleum ether = 1:5) to afford the desired product 3aa (59% yield and 69% *ee* from 2a-1, 55% yield and 72% *ee* from 2a-2).

Tetrabutyl ammonium decatungstate (TBADT) (33.2 mg, 0.01 mmol, 5 mol%), Ni(ClO₄)₂·6H₂O (11.0 mg, 0.03 mmol, 15 mol%), ligand **L1** (12.8 mg, 0.036 mmol, 18 mol%), NaClO₄ (12.2 mg, 0.1 mmol, 0.5 equiv), and the oxime ester **2a** (51.4 mg, 0.2 mmol, 1 equiv) were placed in an oven-dried test tube equipped with a magnetic stir bar. The tube was evacuated and filled with nitrogen (three cycles). To these solids, dry MeCN (1 mL, 0.2 M) and cyclohexa-1,4-diene (57 μL, 0.6 mmol, 3 equiv) were added

under nitrogen atmosphere, successively. Subsequently, the reaction mixture was stirred and irradiated using two 34 W 390 nm LED lamps (Kessil PR160-390, 5 cm away, with adequate fans and a water bath to keep the reaction at room temperature) for 24h. After exposing to air for 15 minutes, the reaction mixture was filtered through a pad of Celite and concentrated under reduced pressure. The residue was purified through column chromatography on silica gel (petroleum ether/ethyl acetate 5:1) to afford (R)-2,4,4-Trimethyl-5-phenyl-3,4-dihydro-2H-pyrrole (3aa') as a colorless oil in 19% yield (7.1 mg) and 16% ee.

¹**H NMR** (400 MHz, Chloroform-*d*) δ = 7.69 (d, *J* = 7.6 Hz, 2H), 7.41 – 7.33 (m, 3H), 4.14 – 4.05 (m, 1H), 2.11 (dd, *J* = 12.4, 6.7 Hz, 1H), 1.51 (dd, *J* = 12.4, 8.6 Hz, 1H), 1.39 (d, *J* = 6.8 Hz, 3H), 1.35 (s, 3H), 1.33 (s, 3H) ppm.

¹³C **NMR** (101 MHz, Chloroform-*d*) δ = 179.4, 134.9, 129.5, 128.3 (2C), 128.0 (2C), 63.3, 51.0, 50.0, 27.6, 26.0, 22.3 ppm.

HRMS (ESI) m/z calculated for $C_{13}H_{17}NH^+$ [M+H]⁺: 188.1439, found: 188.1434.

HPLC-Data: 16% *ee*, (Chiral MD column, $\lambda = 254$ nm, hexane/isopropanol = 95/5, flow rate = 0.5 mL/min): $t_R = 7.8$ (minor), 8.5 (major).

Tetrabutyl ammonium decatungstate (TBADT) (33.2 mg, 0.01 mmol, 5 mol%), NaClO₄ (12.2 mg, 0.1 mmol, 0.5 equiv), and the oxime ester **2a** (51.4 mg, 0.2 mmol, 1 equiv) were placed in an oven-dried test tube equipped with a magnetic stir bar. The tube was evacuated and filled with nitrogen (three cycles). To these solids, dry MeCN (1 mL, 0.2 M) and butanal (**1a**, 55 μL, 0.6 mmol, 3 equiv) were added under nitrogen atmosphere, successively. Subsequently, the reaction mixture was stirred and irradiated using two 34 W 390 nm LED lamps (Kessil PR160-390, 5 cm away, with adequate fans and a water bath to keep the reaction at room temperature) for 24h. After exposing to air for 15 minutes, the reaction mixture was filtered through a pad of Celite and concentrated under reduced pressure. According to TLC and NMR analysis, the product **11** was not observed.

Ni(COD)₂ (27.5 mg, 0.1 mmol, 1.0 equiv), ligand **L1** (35.6 mg, 0.1 mmol, 1 equiv), and the oxime ester **2a** (25.7 mg, 0.1 mmol, 1.0 equiv) were placed in an oven-dried test tube equipped with a stir bar. The tube was evacuated and filled with nitrogen (three cycles). To these solids, dry MeCN (0.5 mL, 0.2 M) was added under nitrogen atmosphere. Subsequently, the reaction mixture was stirred for 30 min at room temperature, before it was quenched by water. The formation of **3aa'** was not observed. The reaction mixture was filtered through a pad of Celite and concentrated under reduced pressure. The residue was purified through column chromatography (silica gel, petroleum ether/ethyl acetate 20:1) to afford *2,2-dimethyl-1-phenylpent-4-en-1-one* (**2a'**) as a colorless oil in 85% yield (15.9 mg).

¹**H NMR** (400 MHz, Chloroform-*d*) δ = 7.65 (d, J = 8.0 Hz, 2H), 7.45 (t, J = 7.3 Hz, 1H), 7.39 (t, J = 7.3 Hz, 2H), 5.79 – 5.66 (m, 1H), 5.07 – 4.97 (m, 2H), 2.49 (d, J = 7.3 Hz, 2H), 1.32 (s, 6H) ppm.

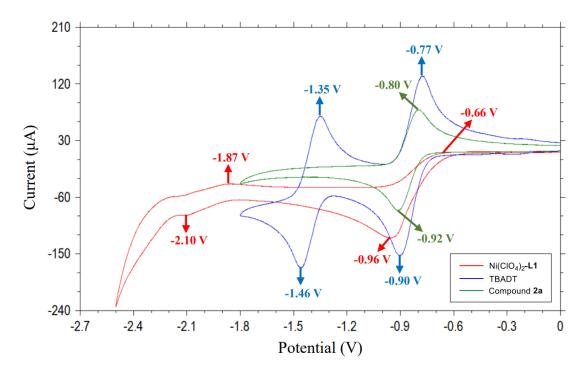
¹³C **NMR** (101 MHz, Chloroform-*d*) δ = 208.9, 139.2, 134.2, 130.9, 128.2 (2C), 127.7 (2C), 118.3, 47.8, 45.1, 25.9 (2C) ppm.

HRMS (ESI) m/z calculated for $C_{13}H_{16}OH^{+}$ [M+H]⁺: 189.1274, found: 189.1275.

Cyclic Voltammetry Experiments

The following experiments were conducted on an electrochemical workstation CHI 760D. A glassy carbon working electrode (0.07 cm²) was employed alongside a platinum flag counter electrode and an Ag/AgCl (KCl sat.) reference electrode. The distance between the working and reference electrode was 1 cm. The polishing material is 50 nm α-aluminum oxide, and the solvent was degassed through purging with nitrogen atmosphere. The solution of TBADT (10 mM), compound 2a (10 mM), or [Ni(ClO₄)₂·6H₂O + L1] (30 mM) [In a 15-mL vial equipped with a stirring bar, the ligand L1 (53.5 mg, 0.15 mmol) and Ni(ClO₄)₂·6H₂O (54.9 mg, 0.15 mmol) were

charged in a glovebox, before anhydrous MeCN (5 ml) was added. The mixture was stirred at room temperature for 0.5 h. The resulting solution was used in cyclic voltammogram studies without further purification.] in MeCN along with 0.1 M supporting electrolyte (tetrabutylammonium hexafluorophosphate) was tested at room temperature with the initial potential of 0 V and scan rate of 0.1 V/s (IUPAC, negative scan), respectively.

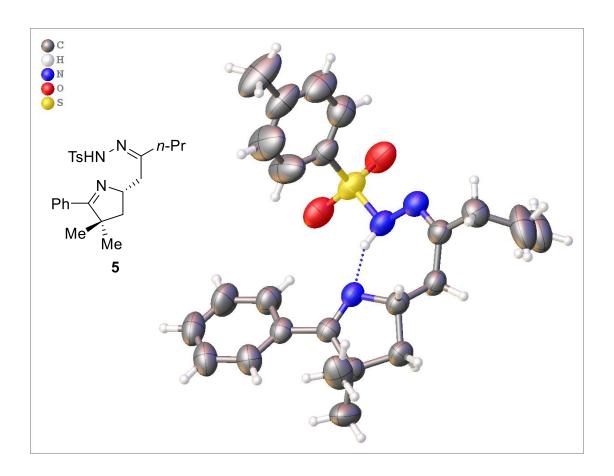


Cyclic voltammograms of [Ni(ClO₄)₂·6H₂O+L1] (Red), TBADT (Blue), and compound 2a (Green) in MeCN

Crystal Data and Structural Refinement

CCDC 2246373 contains the supplementary crystallographic data for the compound 5.

These data can be obtained free of charge from The Cambridge Crystallographic Data Centre.



Identification code WR-NNHTS_auto

Empirical formula $C_{24}H_{31}N_3O_2S$

Formula weight 425.58

Temperature/K 293(2)

Crystal system Orthorhombic

Space group $P2_12_12_1$

a/Å 9.26014(12)

b/Å 11.7541(2)

c/Å 21.9162(3)

α/° 90

β/° 90

γ/° 90

Volume/Å³ 2385.46(6)

Z 4

 $\rho_{calc}g/cm^3 1.185$

 μ/mm^{-1} 1.388

F(000) 912.0

Crystal size/mm³ $0.22 \times 0.17 \times 0.16$

Radiation Cu K α ($\lambda = 1.54184$)

2Θ range for data collection/° 8.068 to 145.74

Index ranges $-6 \le h \le 11, -11 \le k \le 14, -25 \le 1 \le 27$

Reflections collected 8750

Independent reflections 4615 [$R_{int} = 0.0181$, $R_{sigma} = 0.0256$]

Data/restraints/parameters 4615/0/280

Goodness-of-fit on F² 1.021

Final R indexes [I>= 2σ (I)] $R_1 = 0.0408$, $wR_2 = 0.1181$

Final R indexes [all data] $R_1 = 0.0430$, $wR_2 = 0.1214$

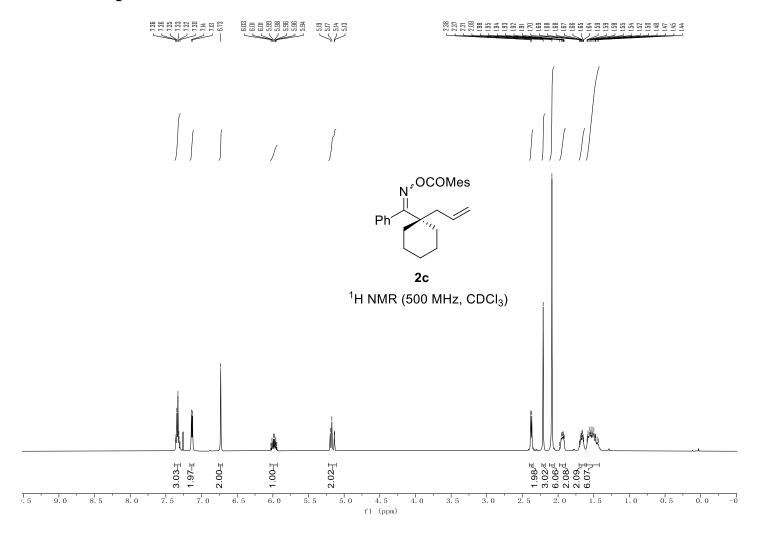
Largest diff. peak/hole / e Å⁻³ 0.29/-0.26

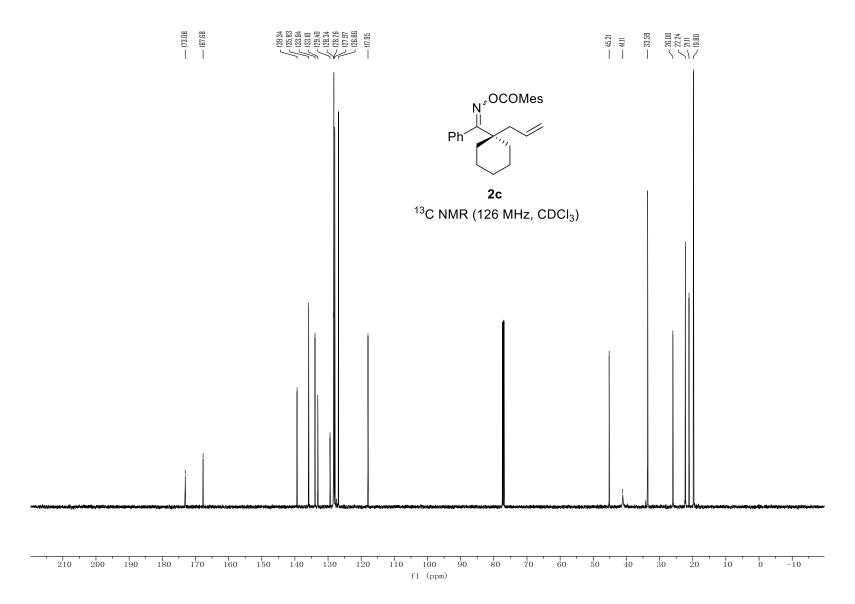
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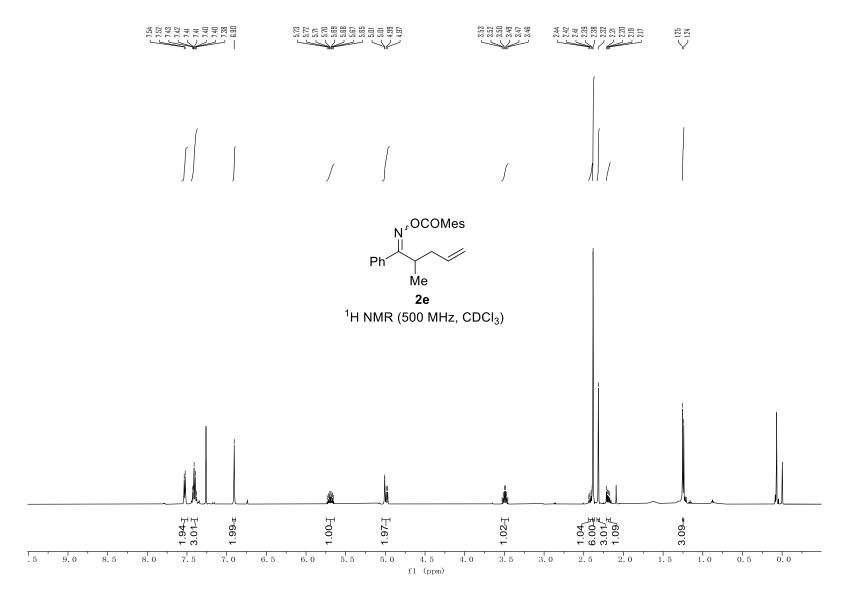
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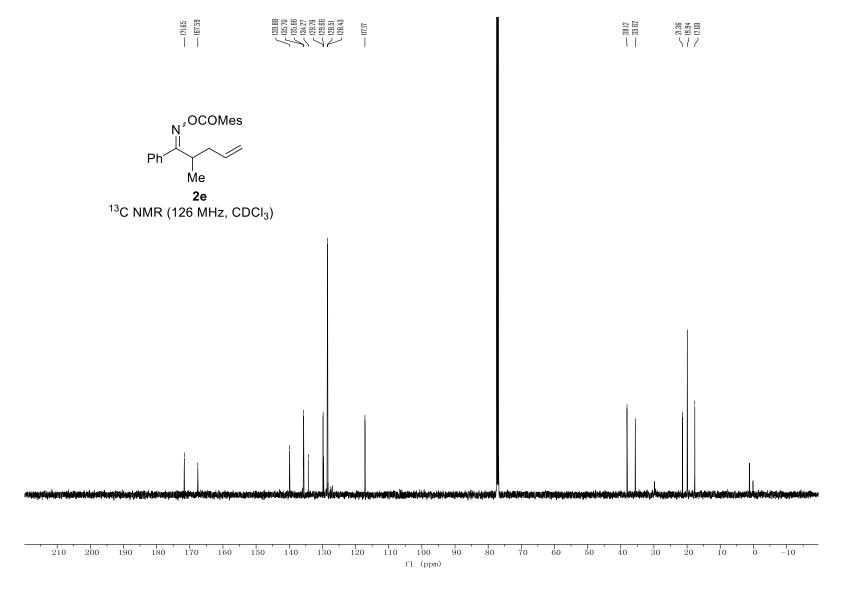
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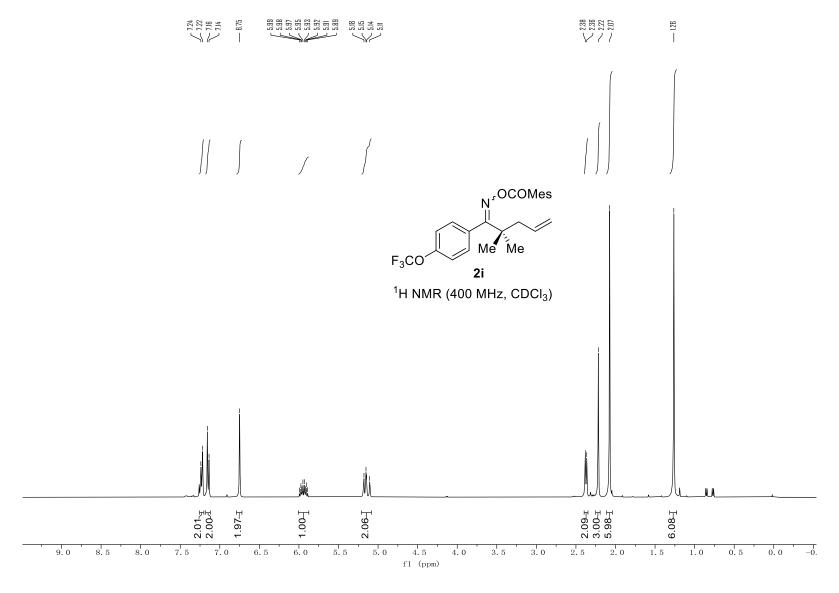
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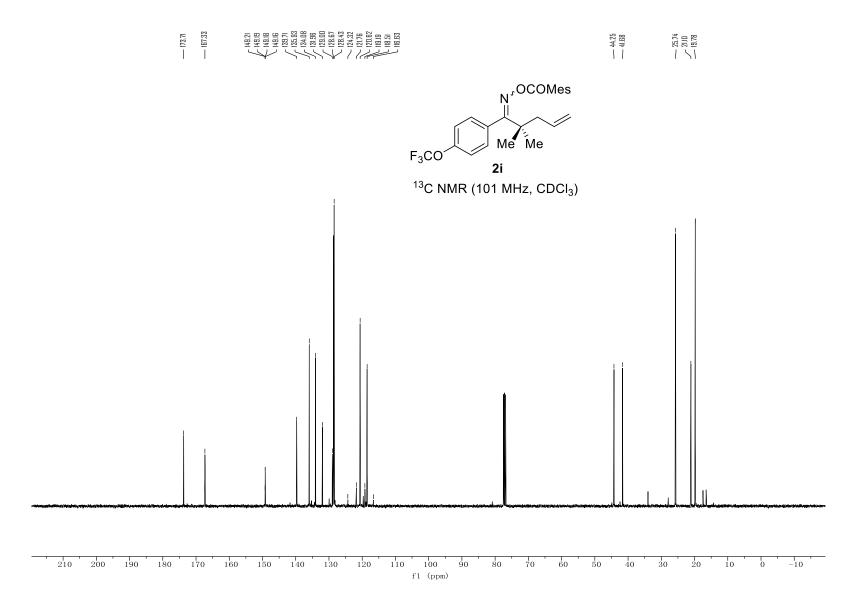


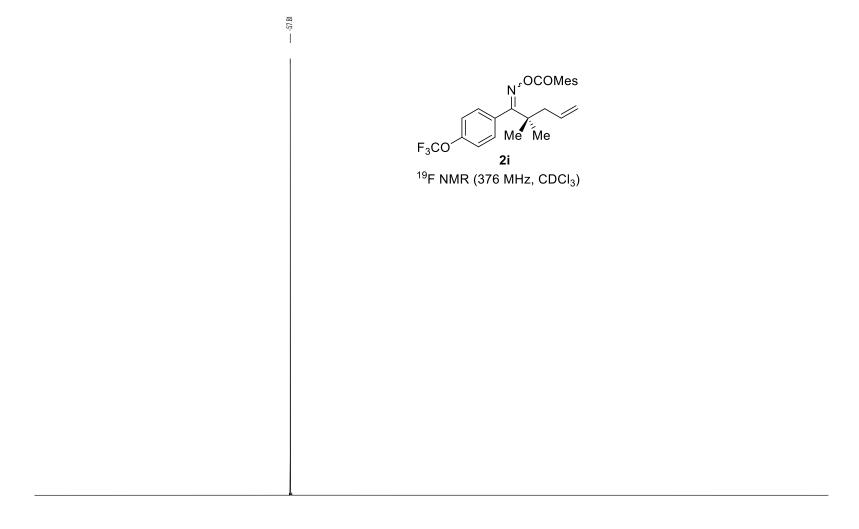


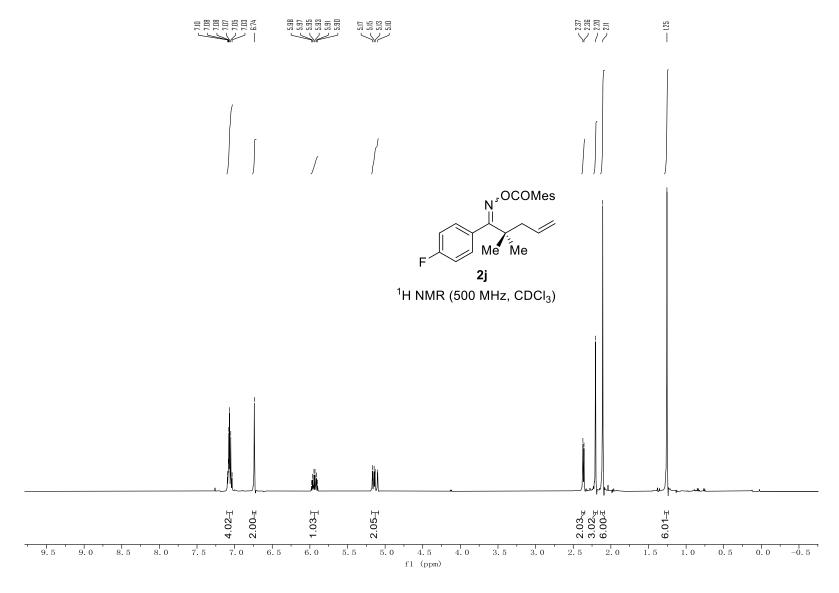


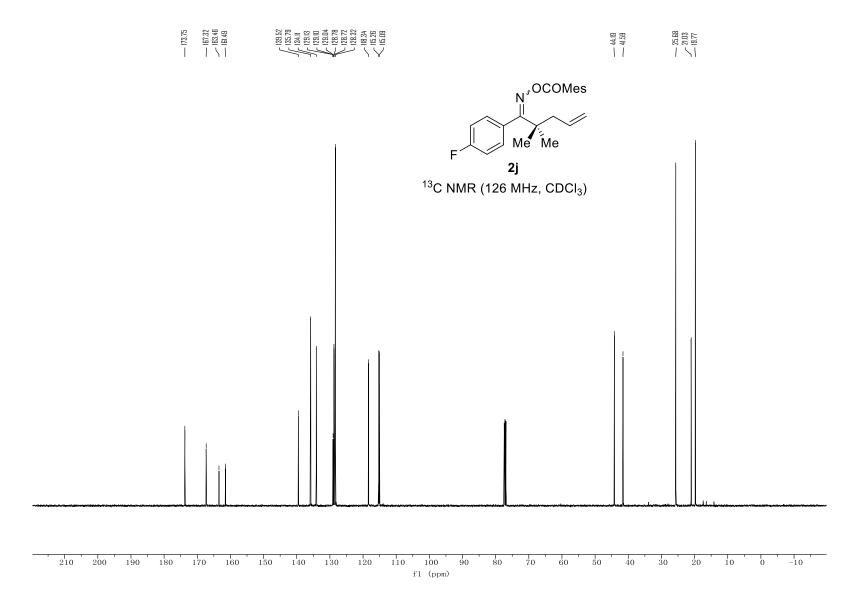


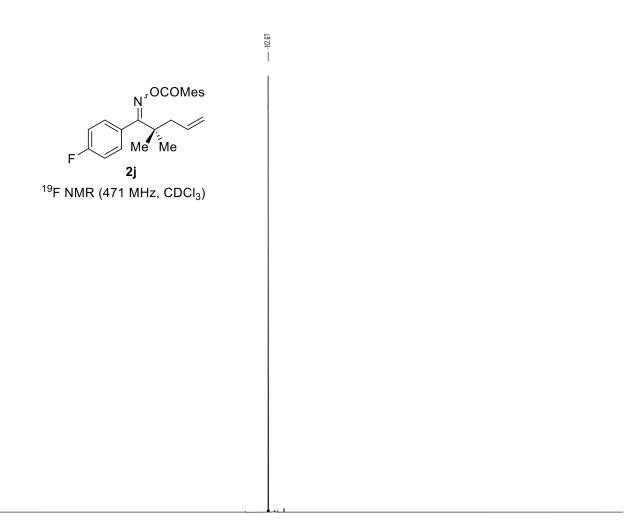


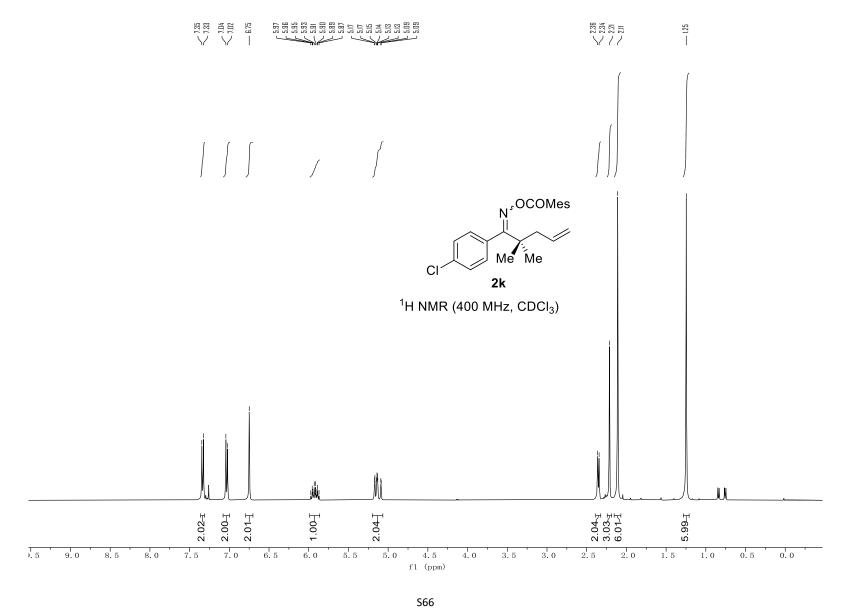


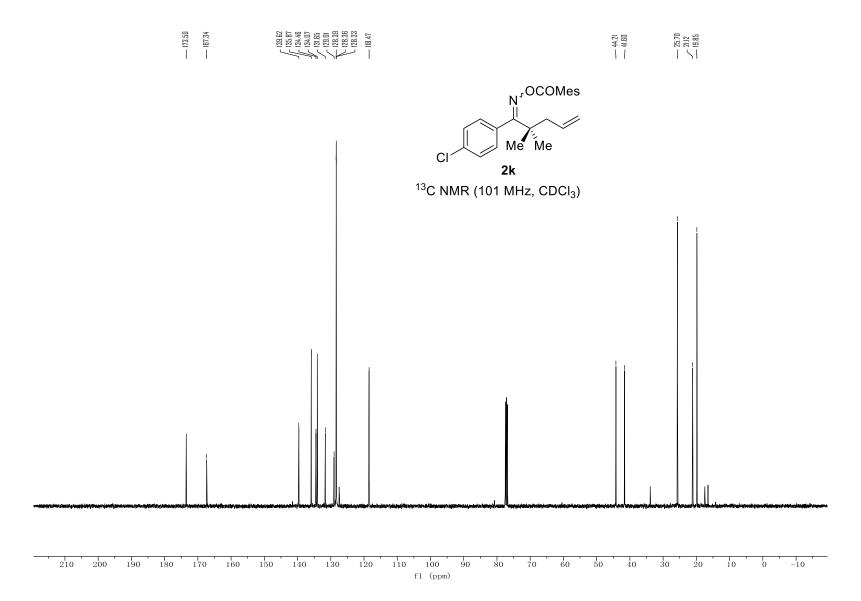


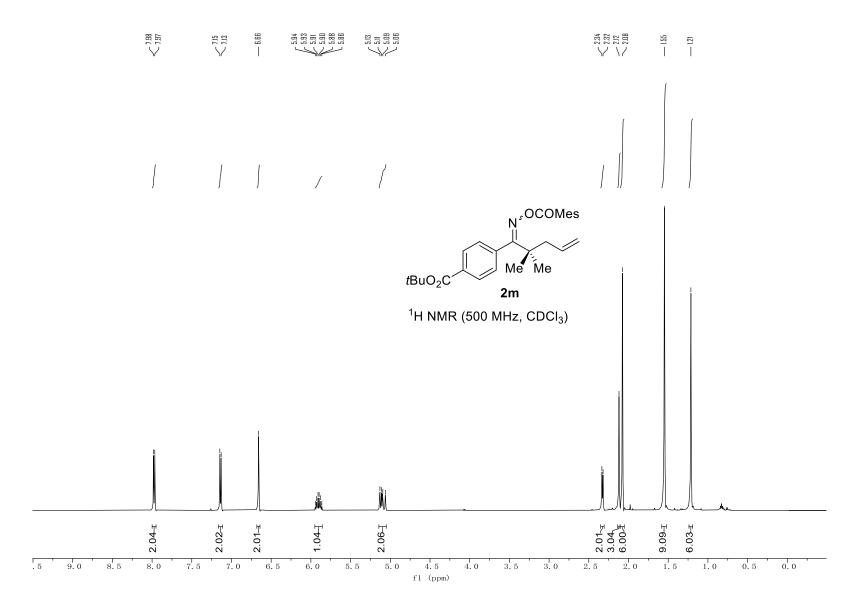


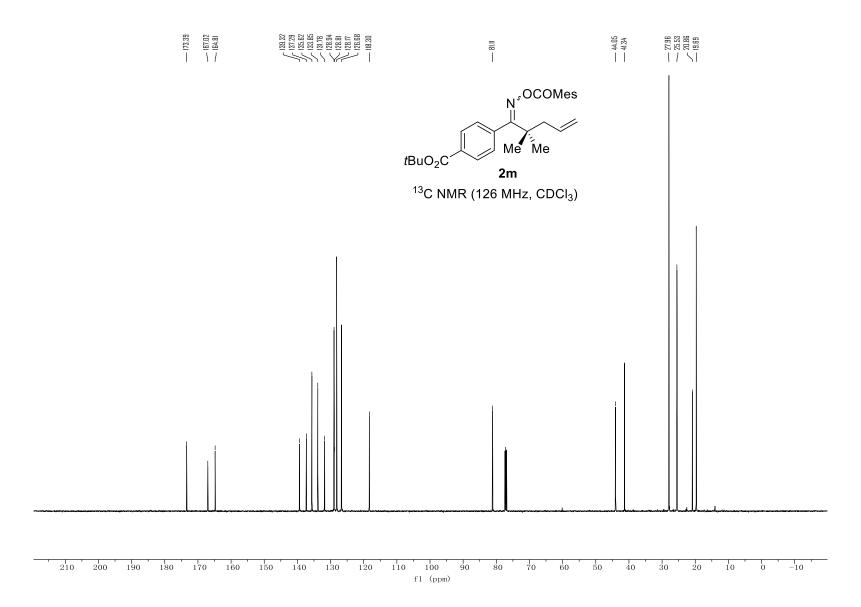


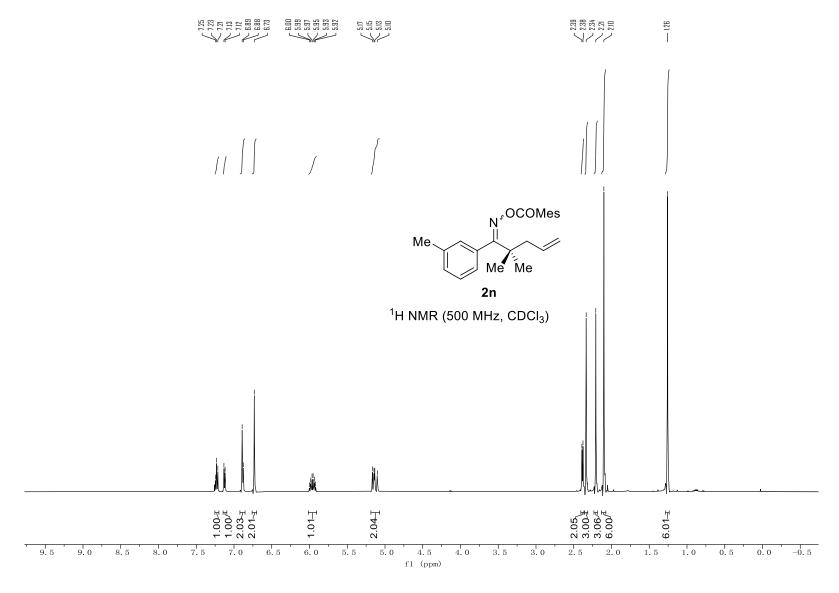


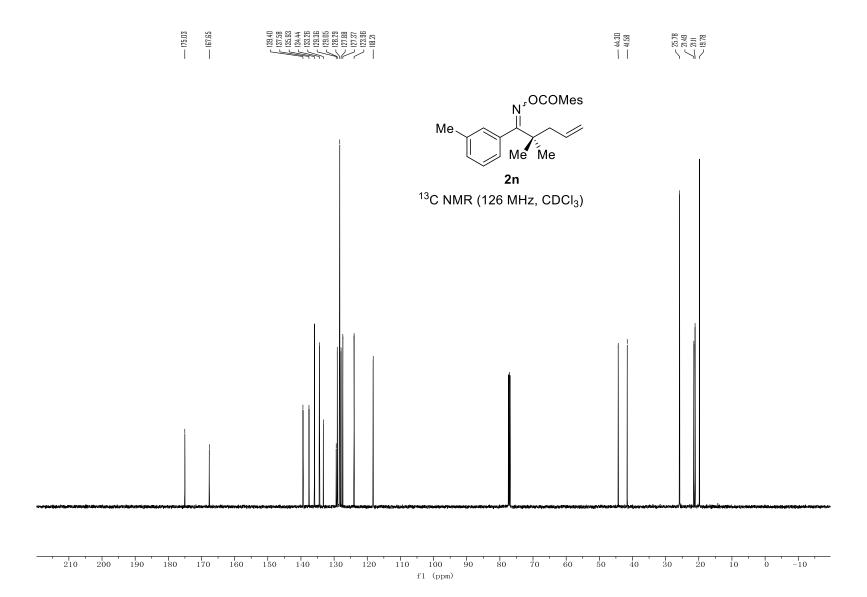


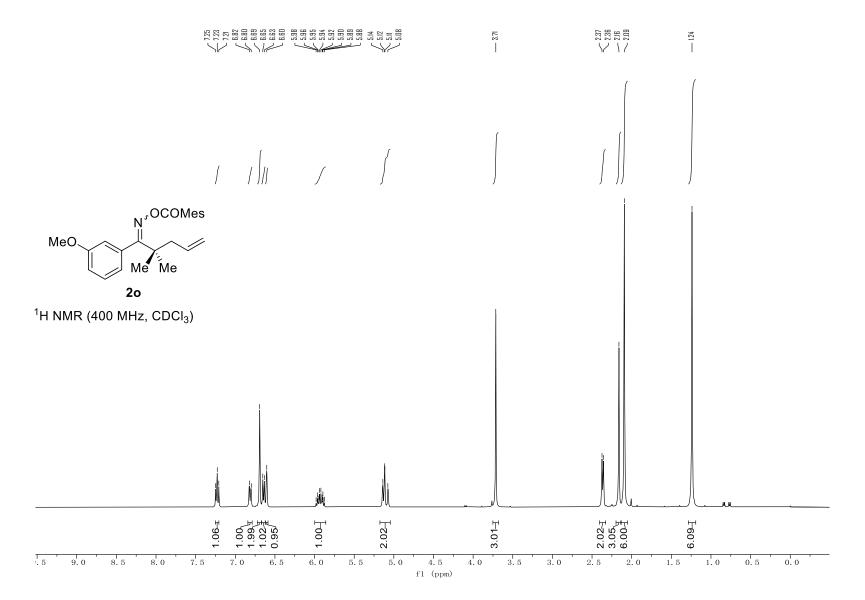


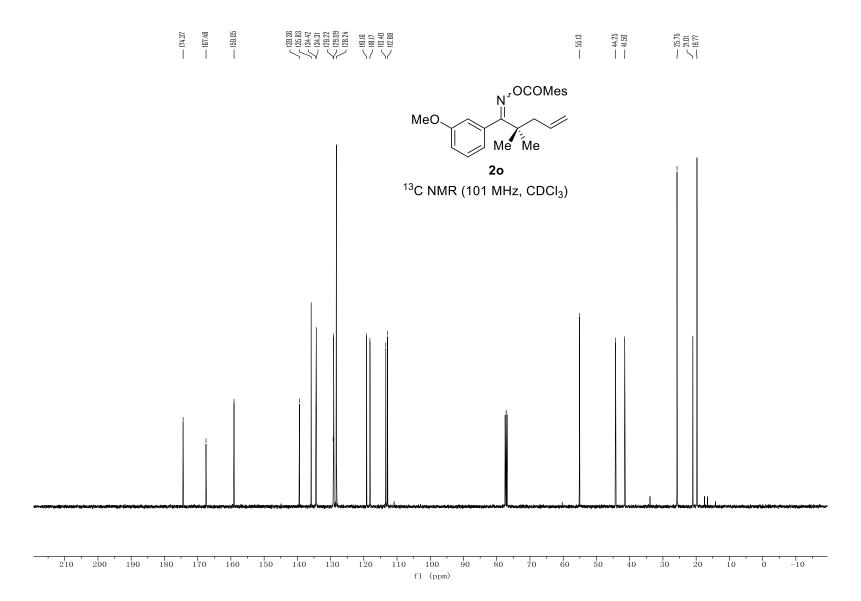


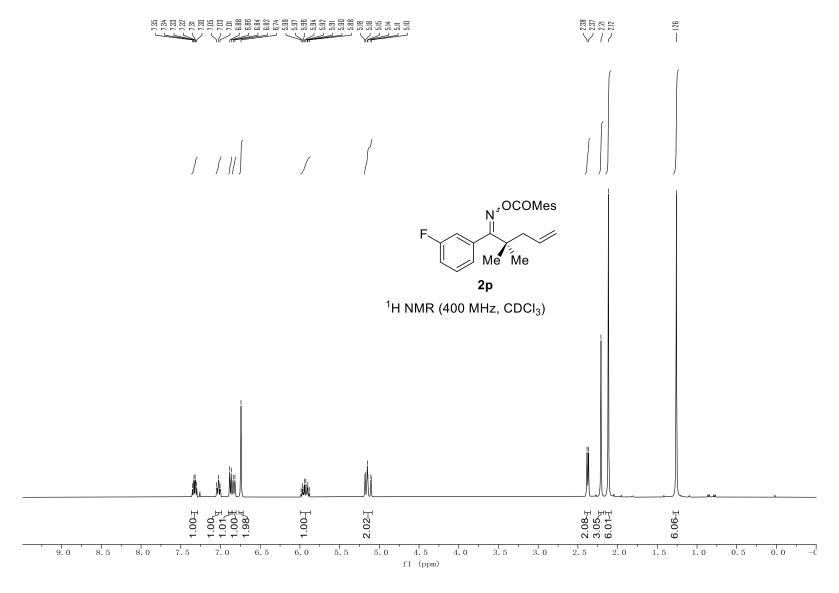


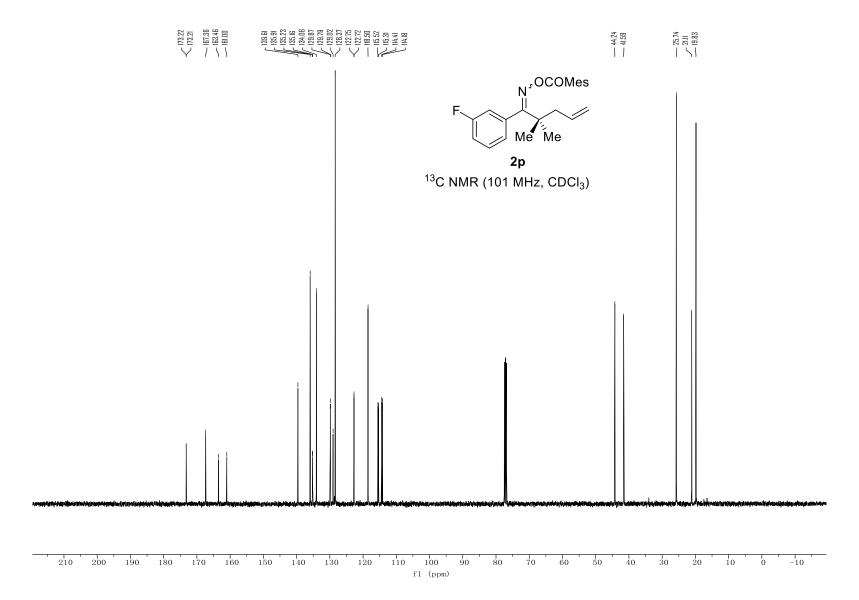


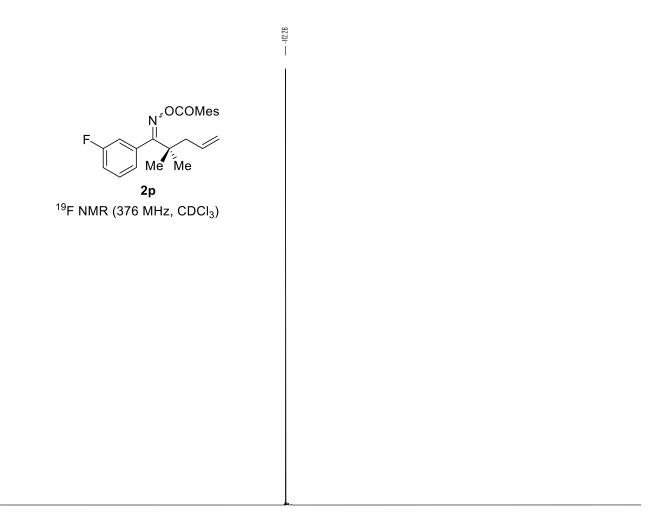


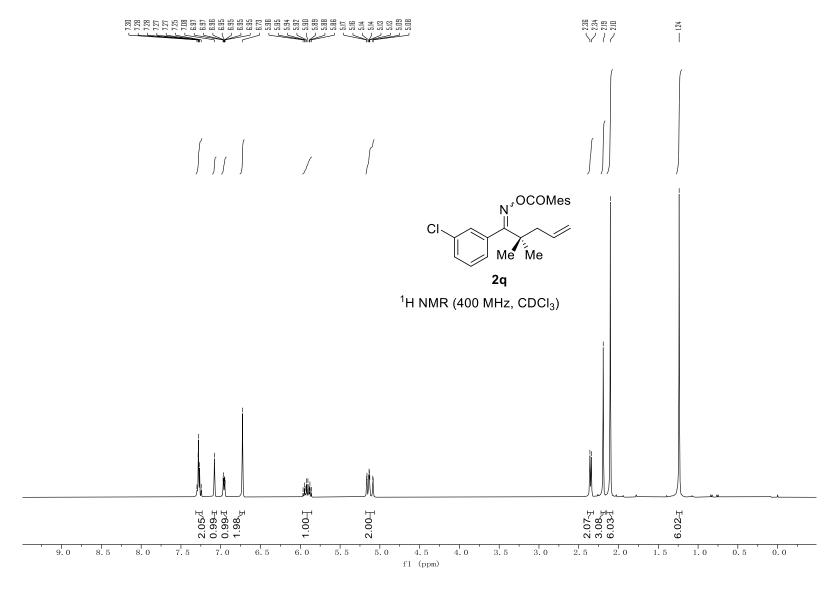


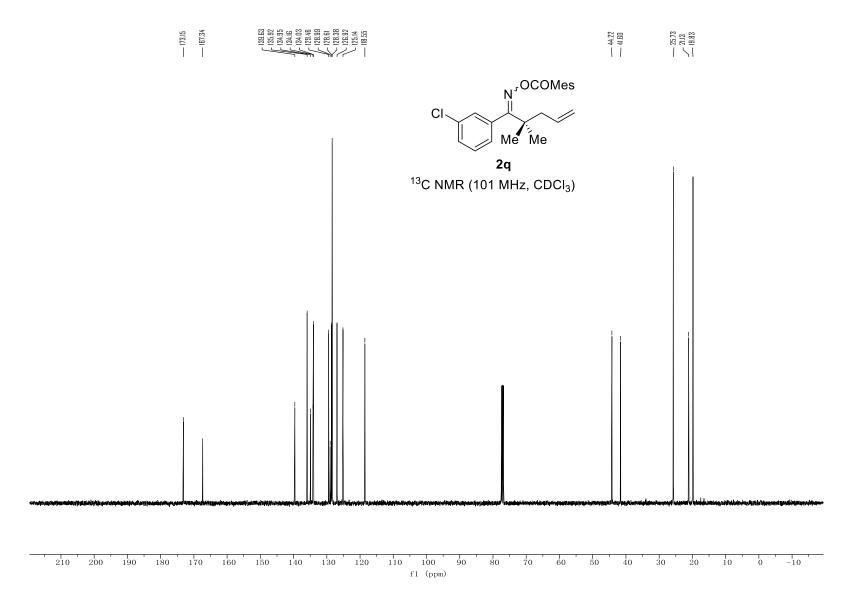


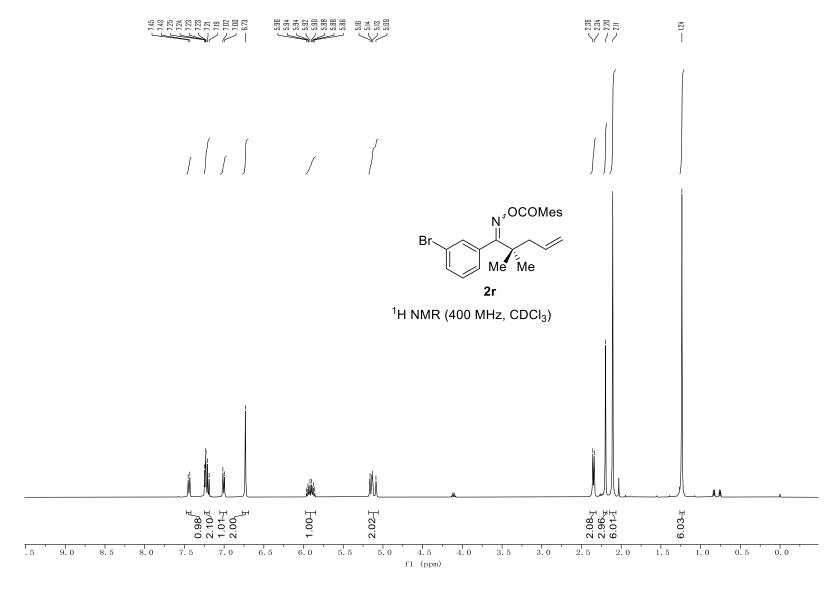


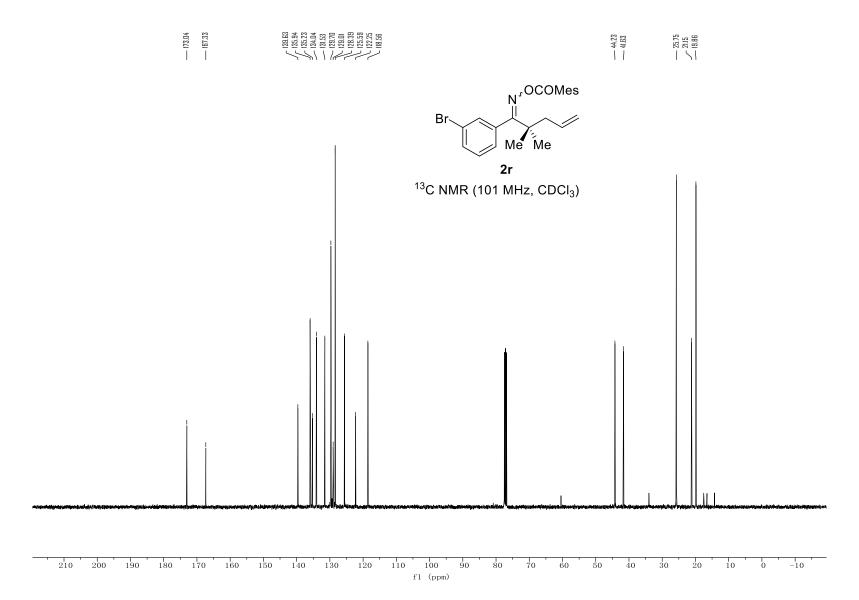


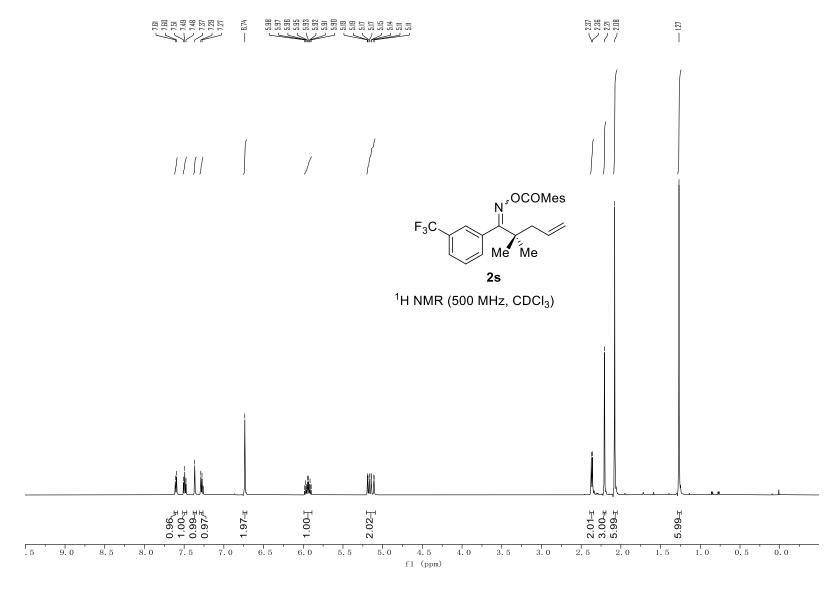


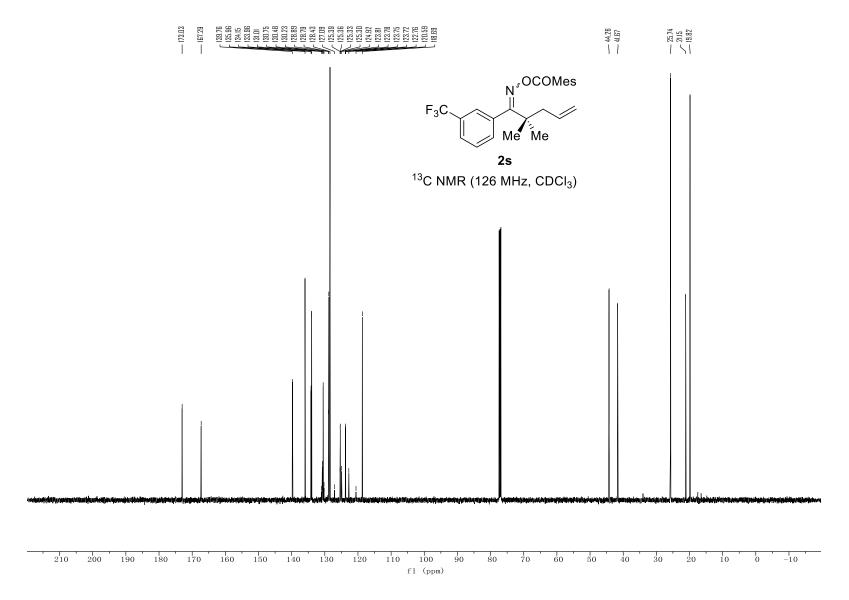


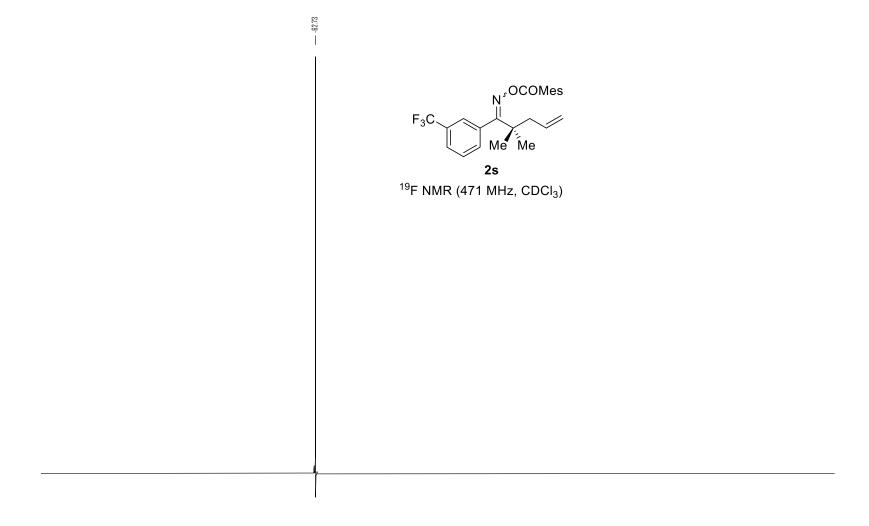




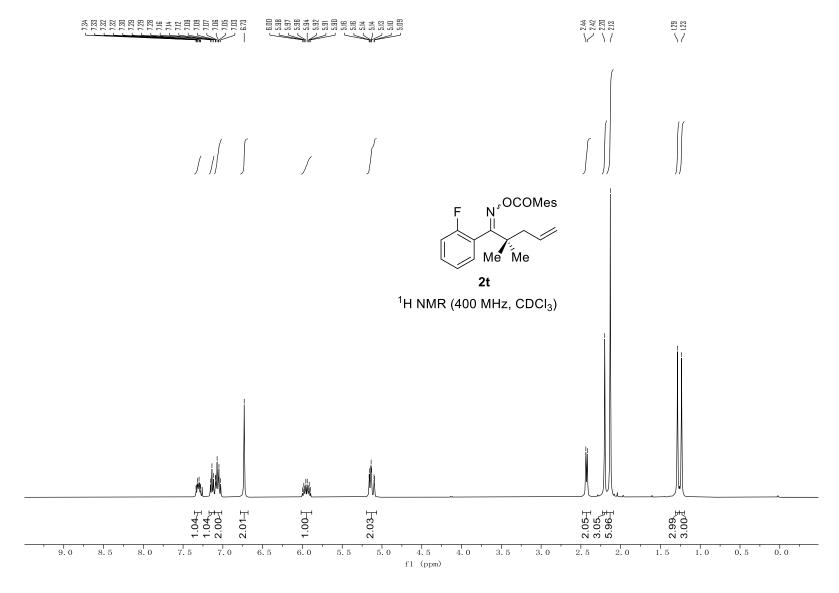


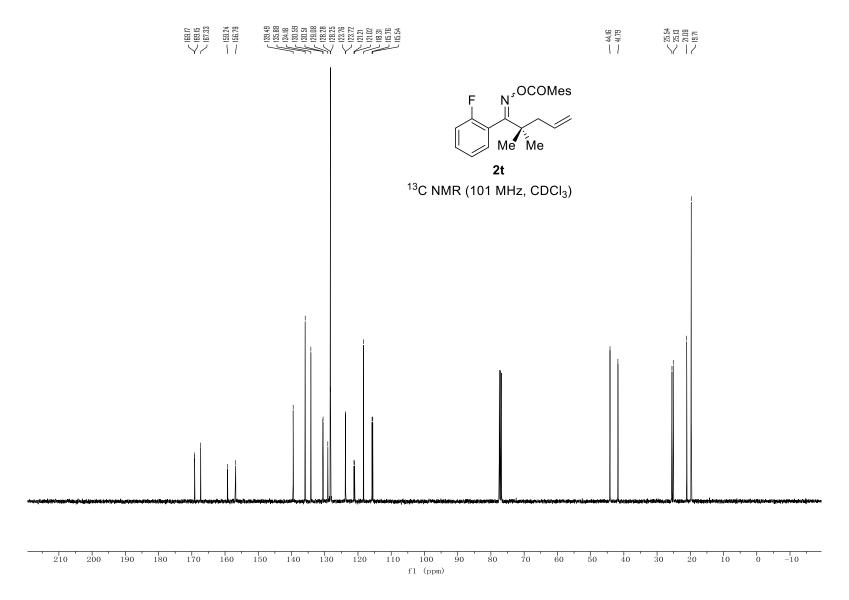


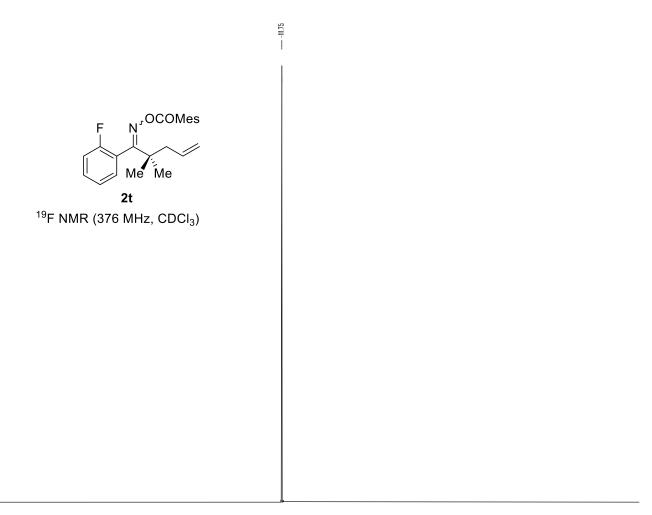


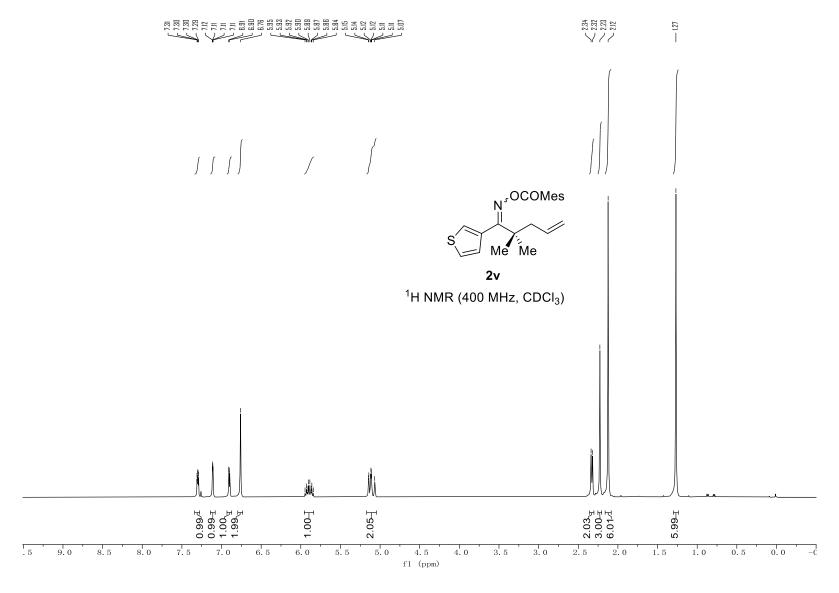


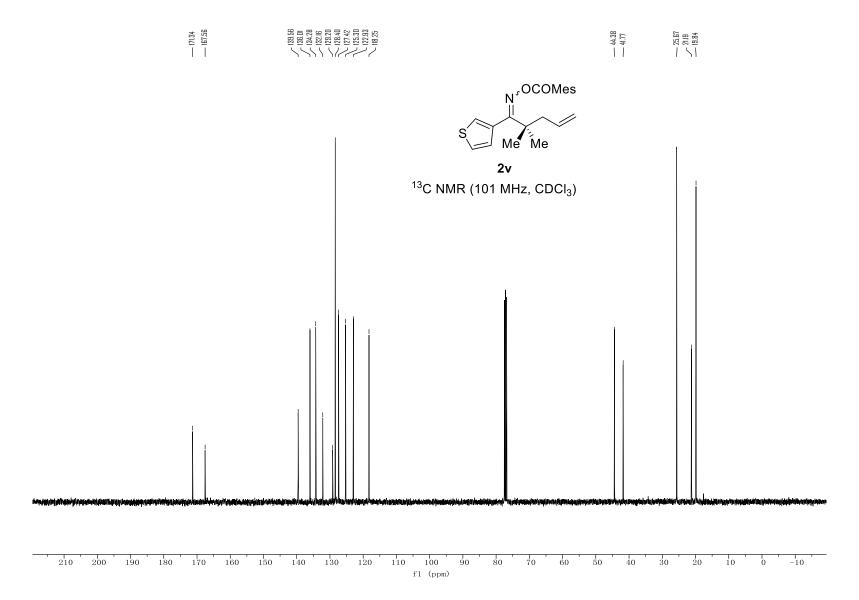
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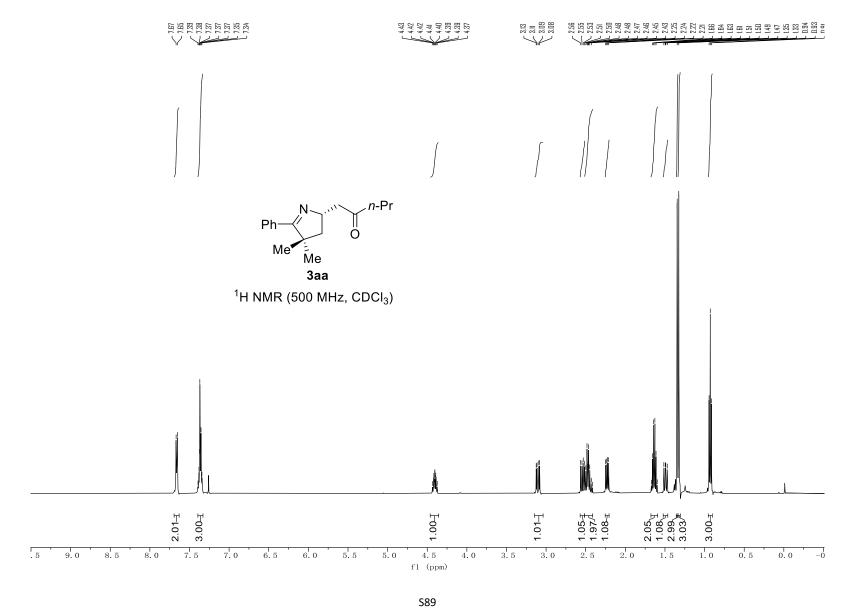


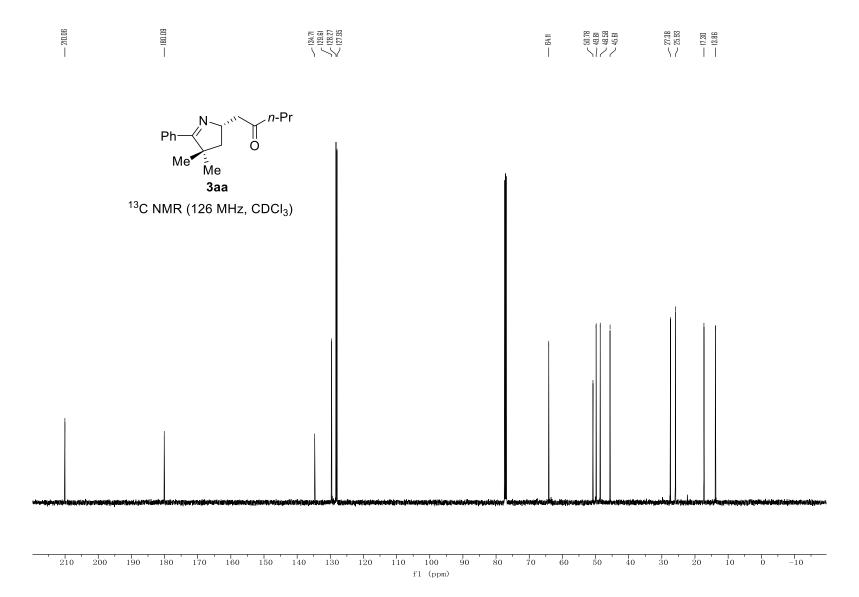


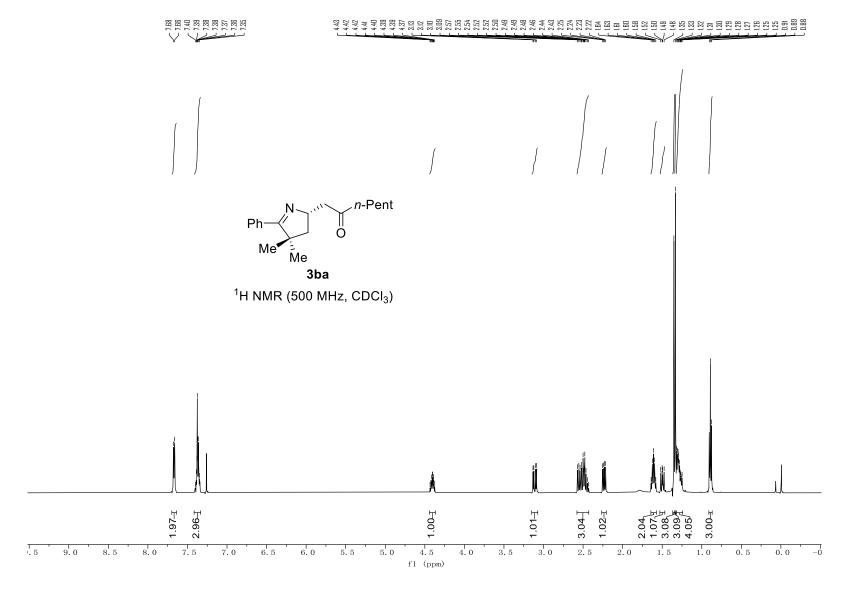


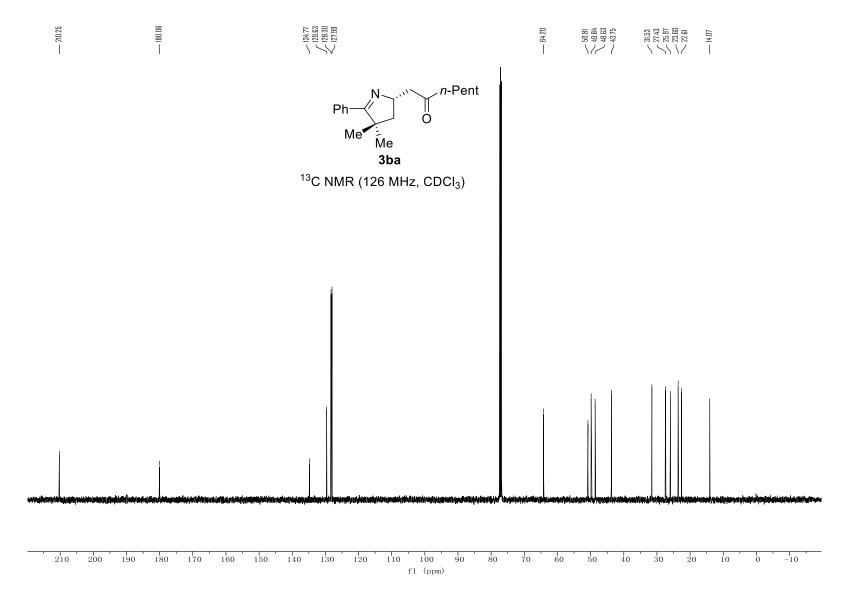


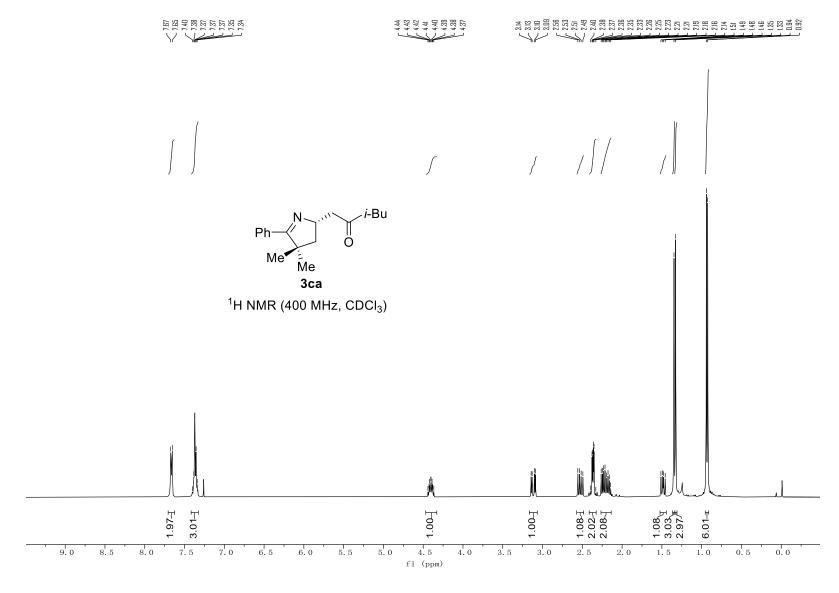


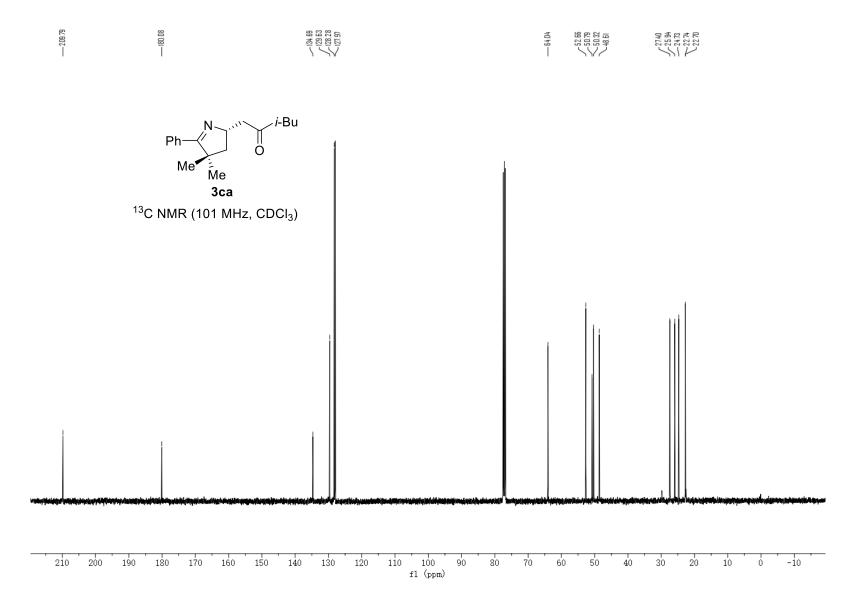


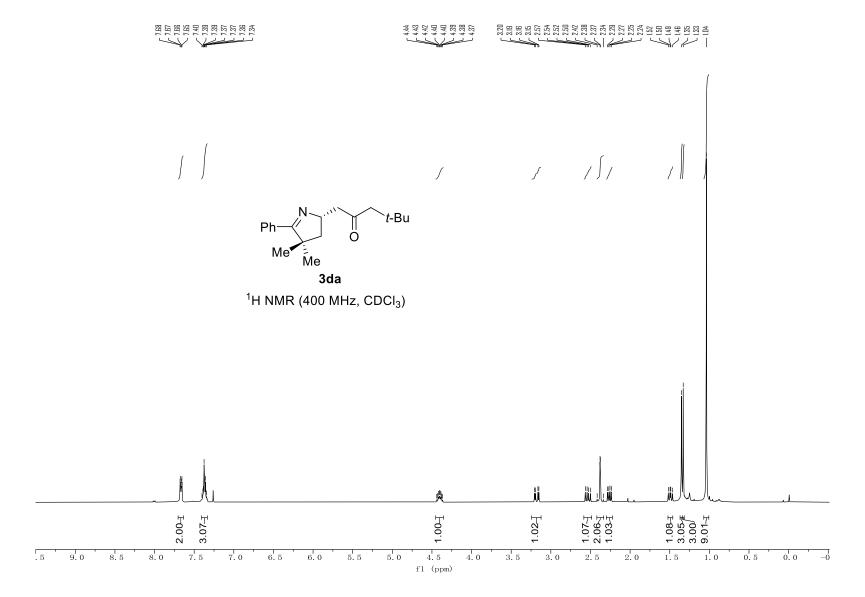


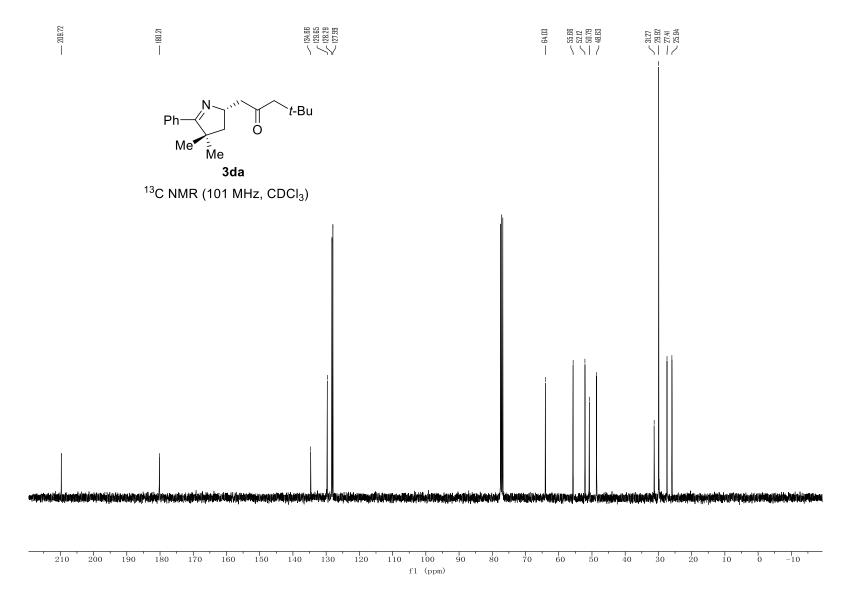


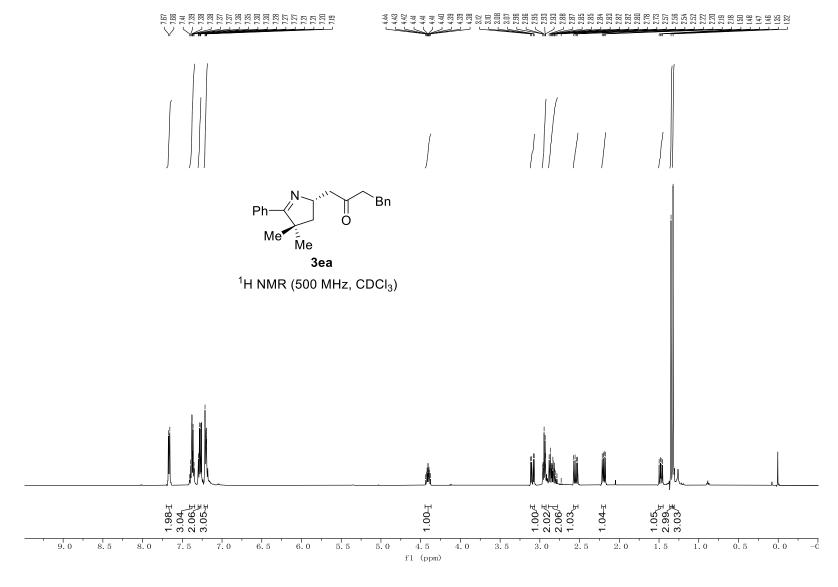


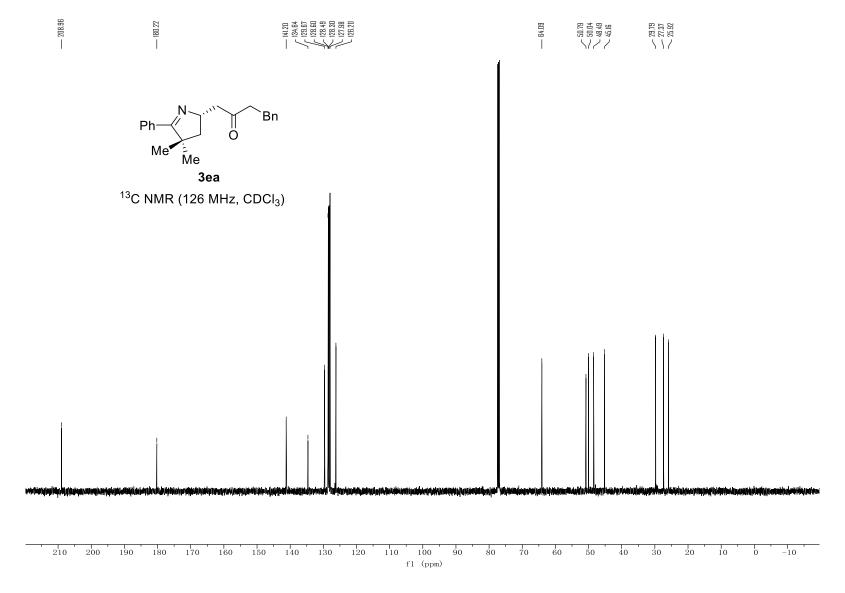


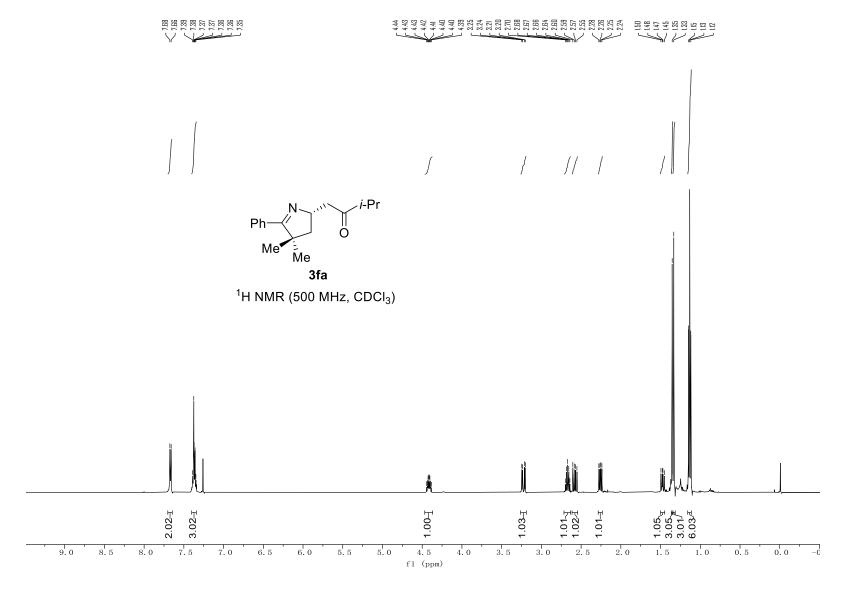


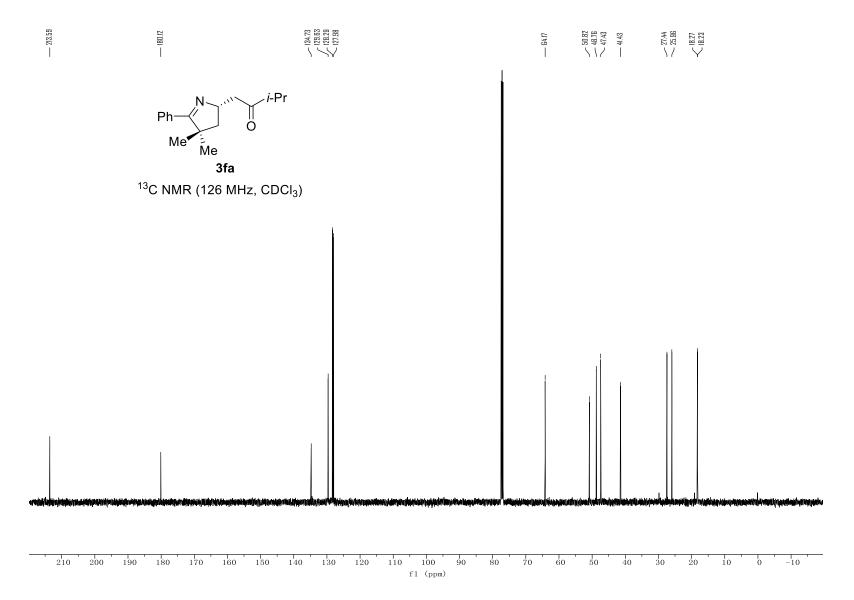


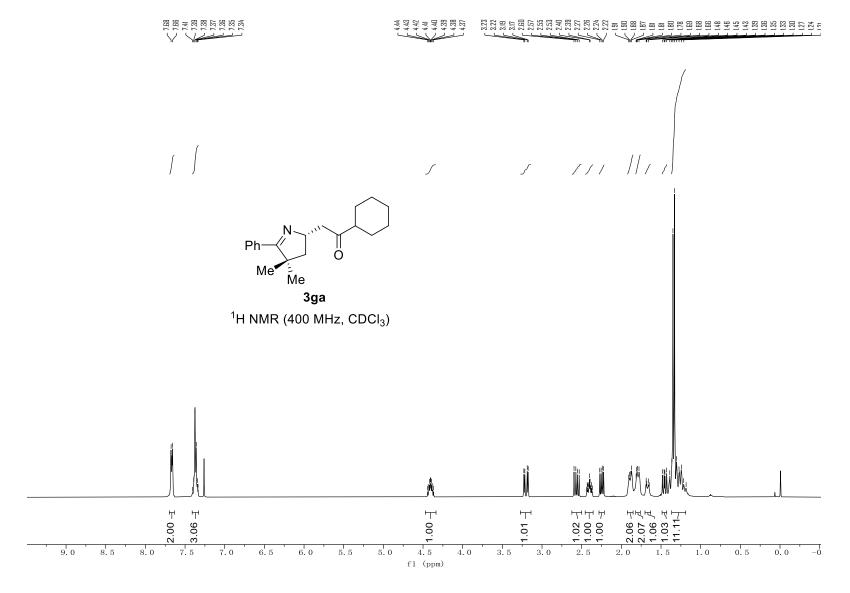


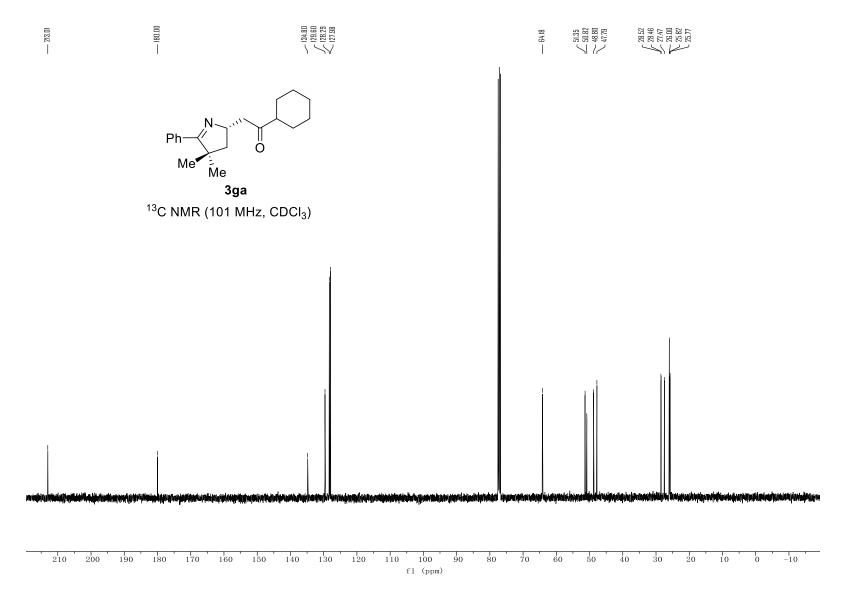


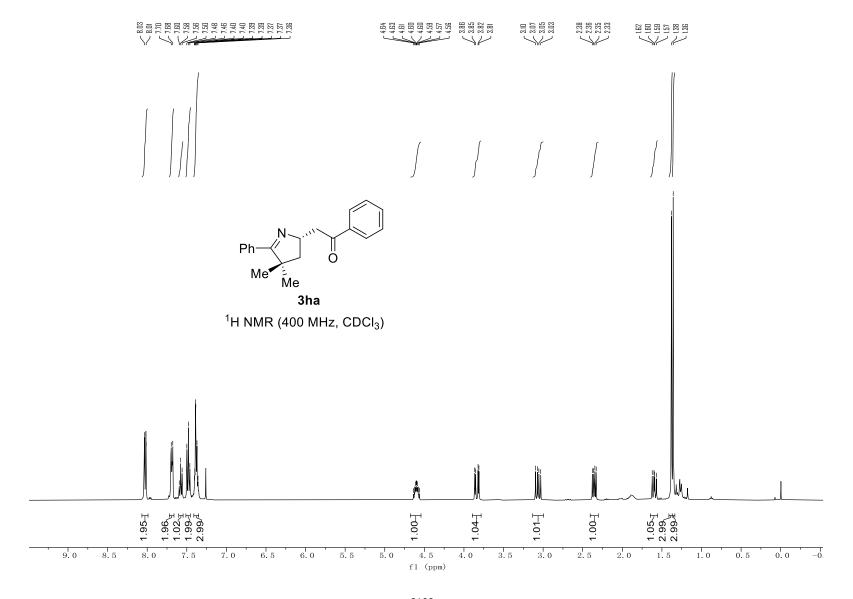


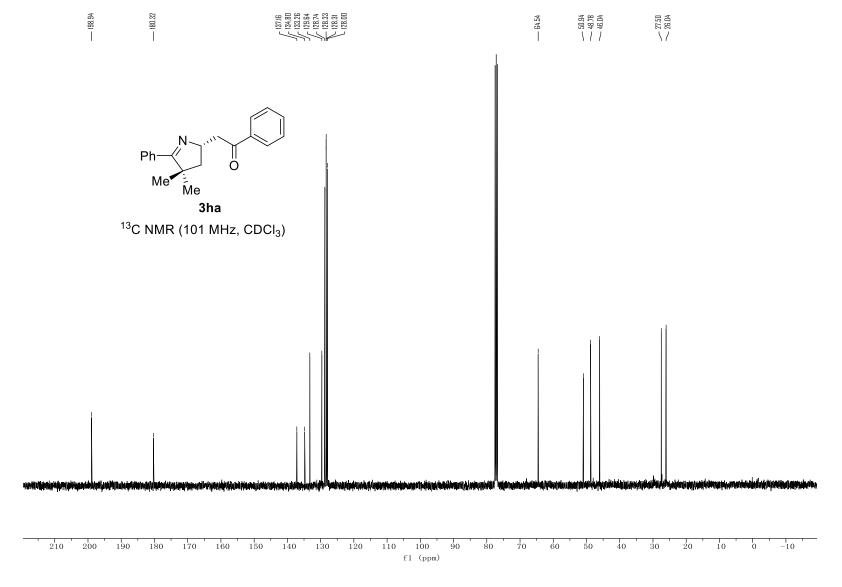


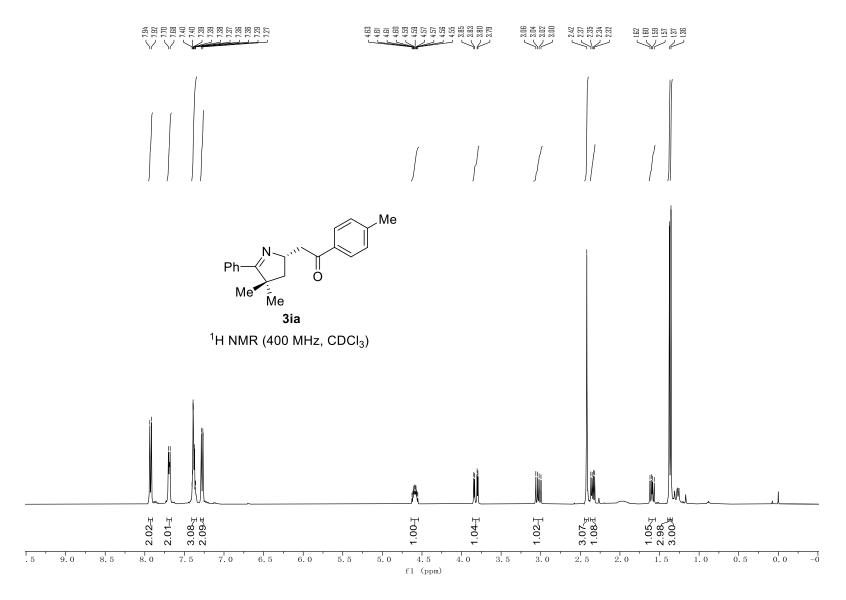


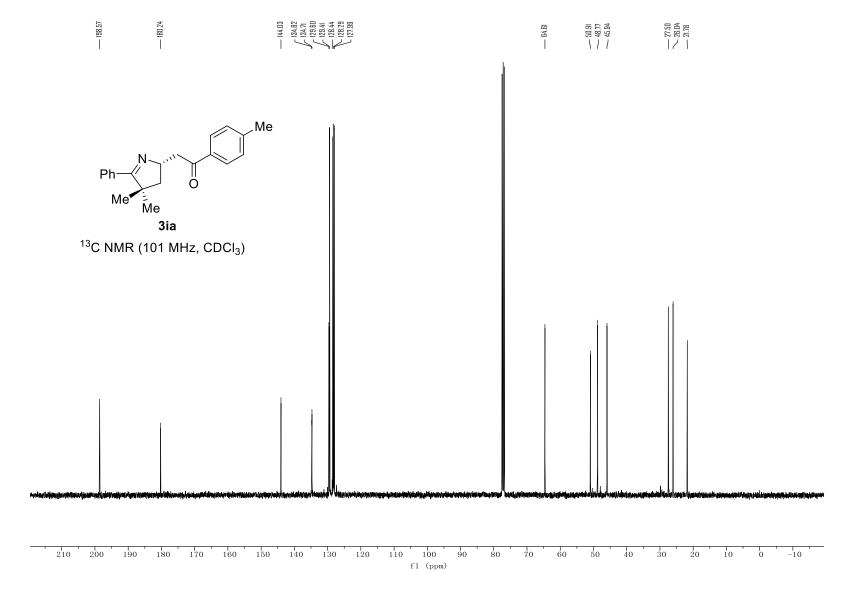


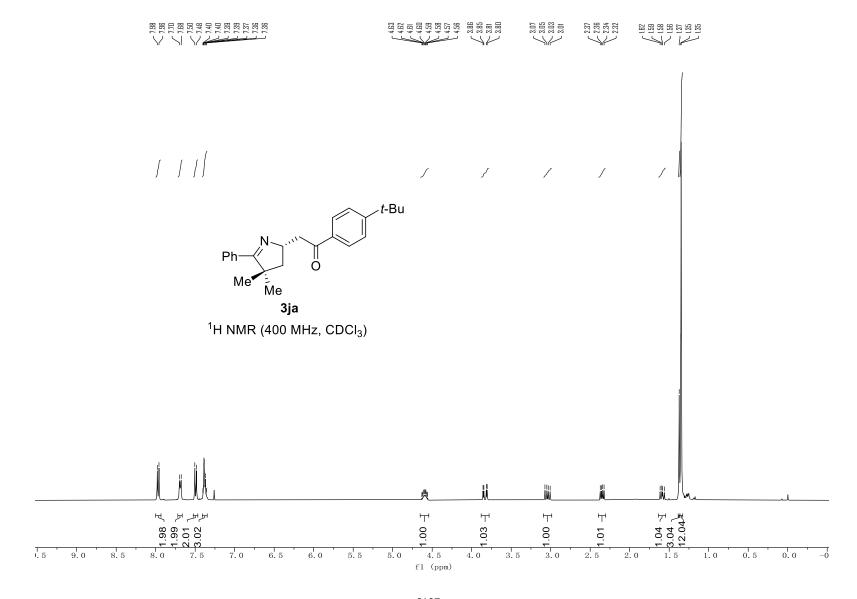


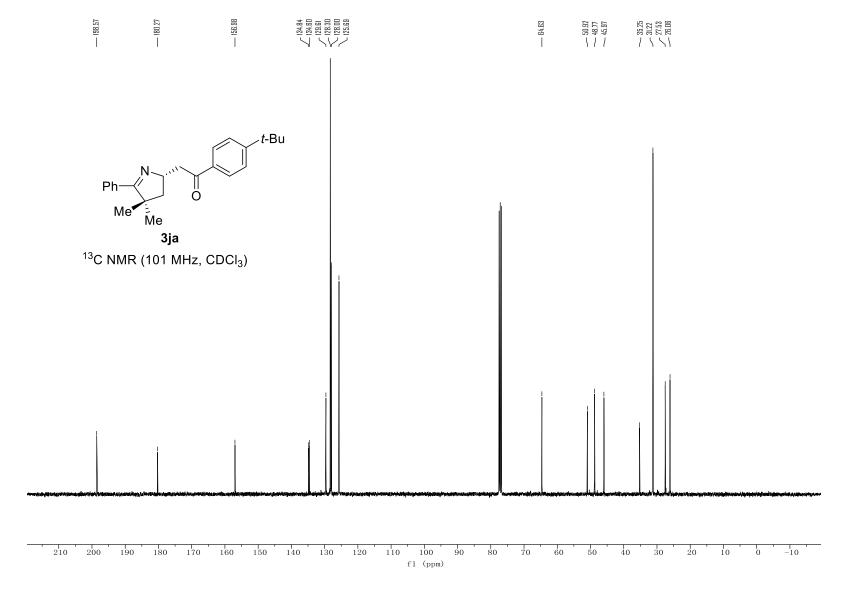


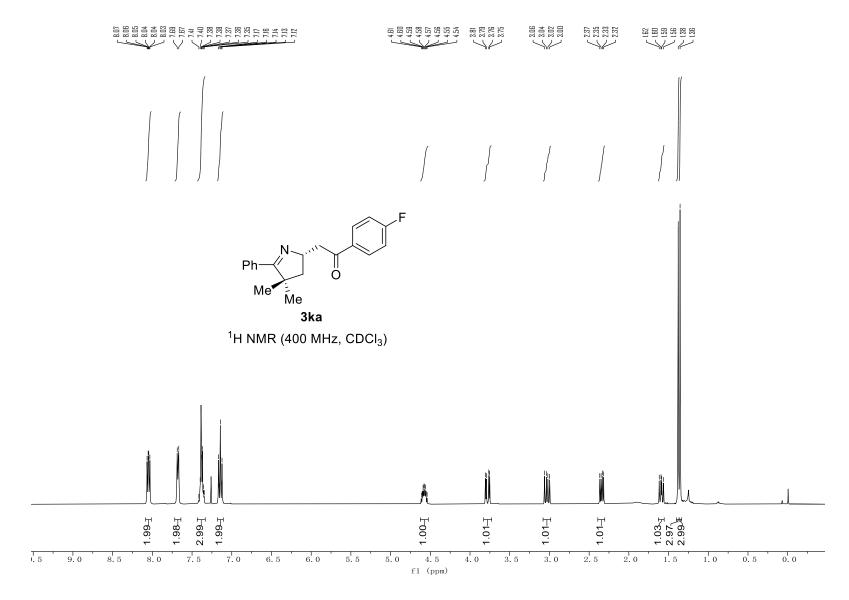


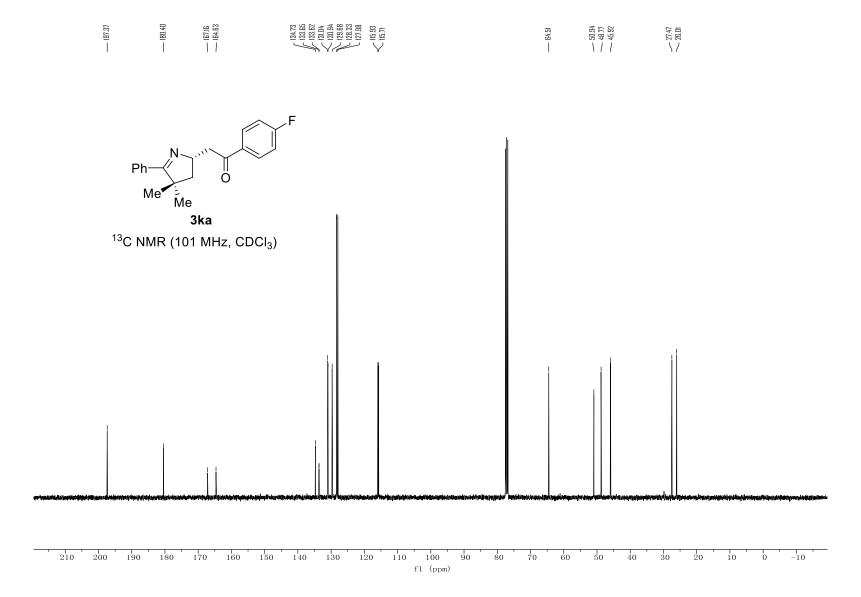


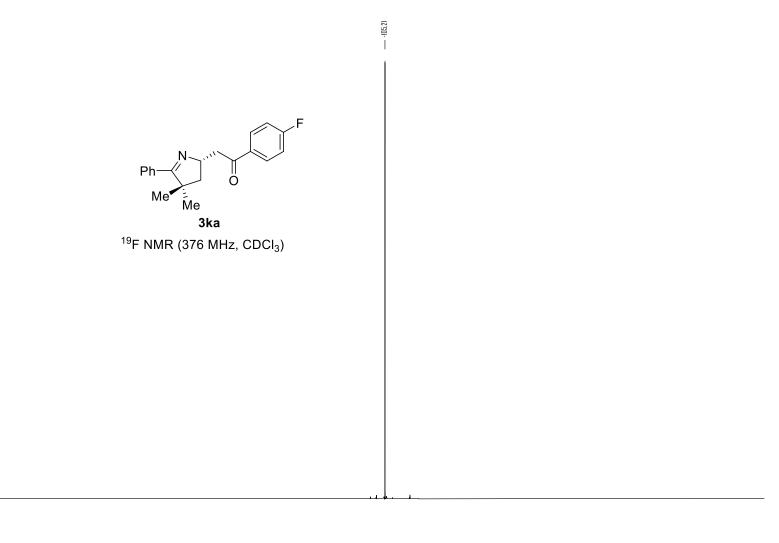


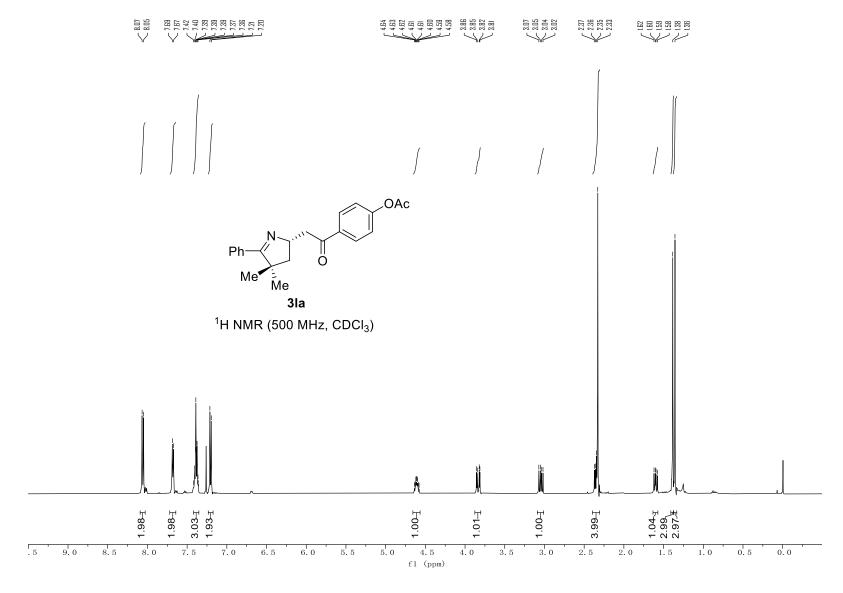


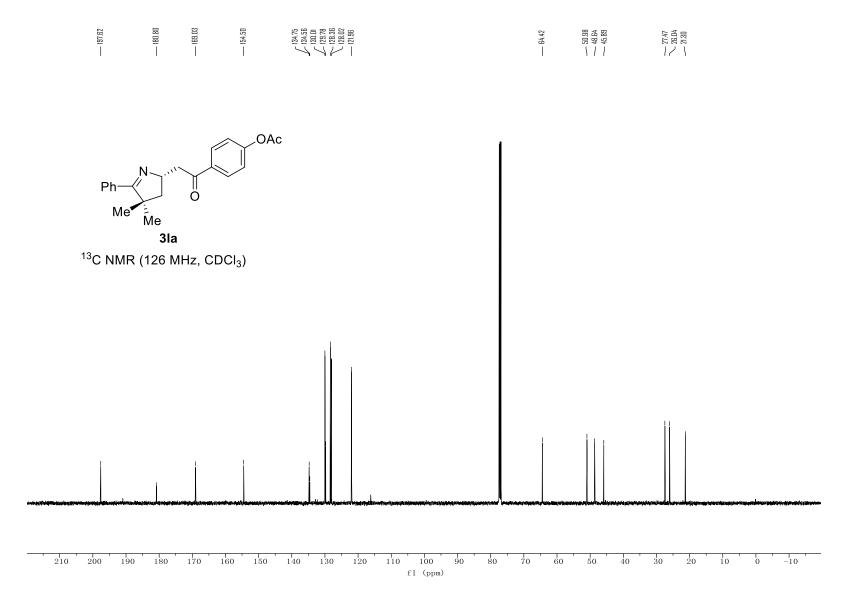


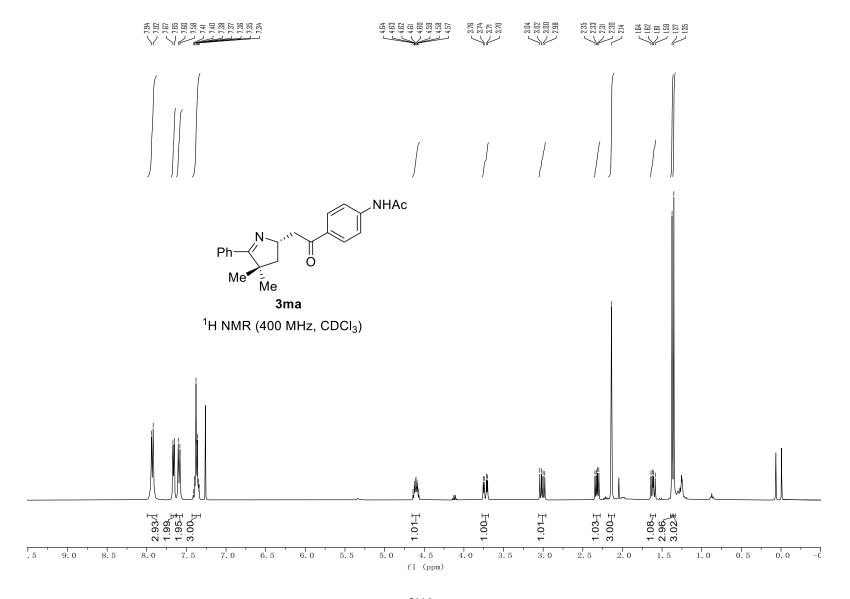


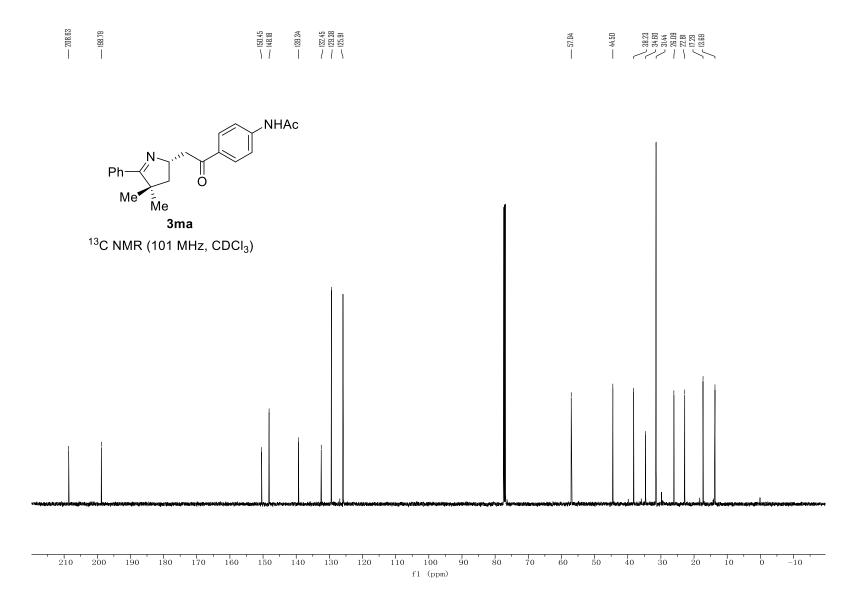


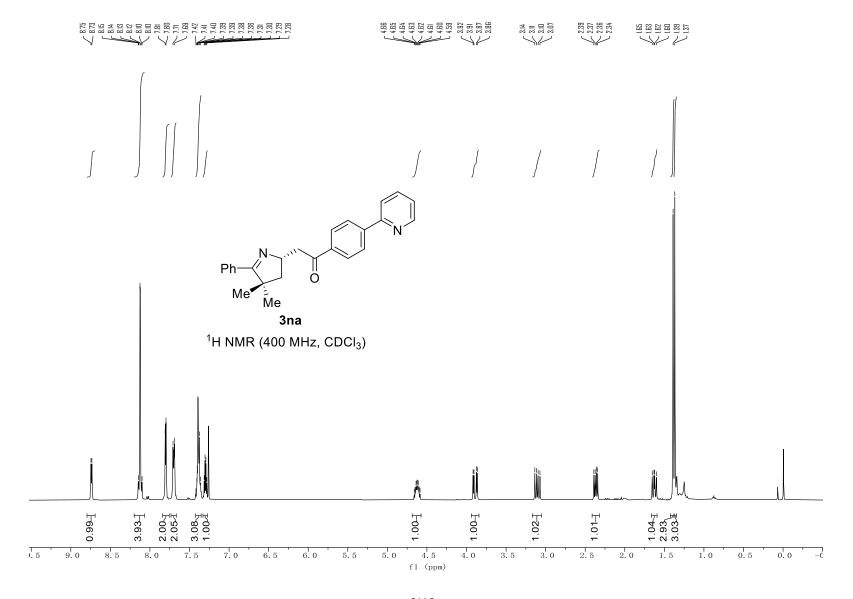


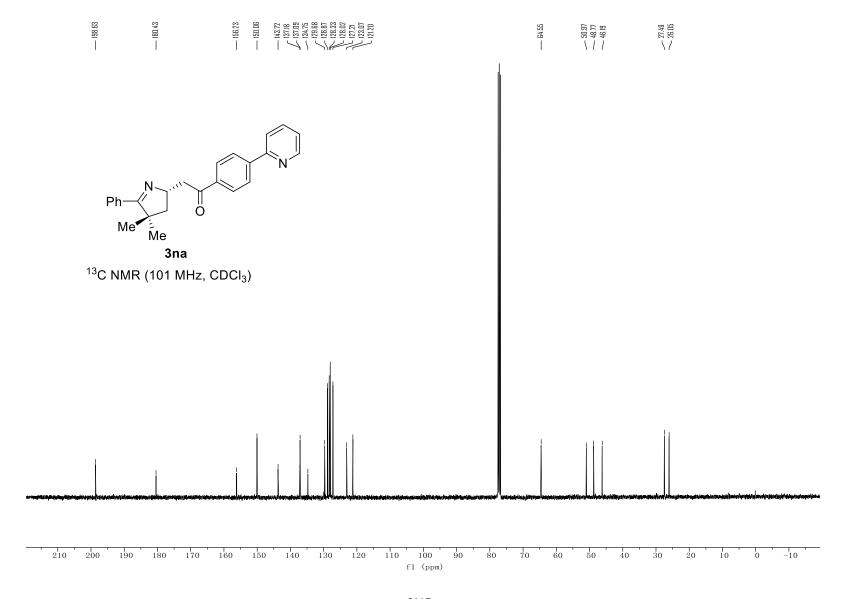


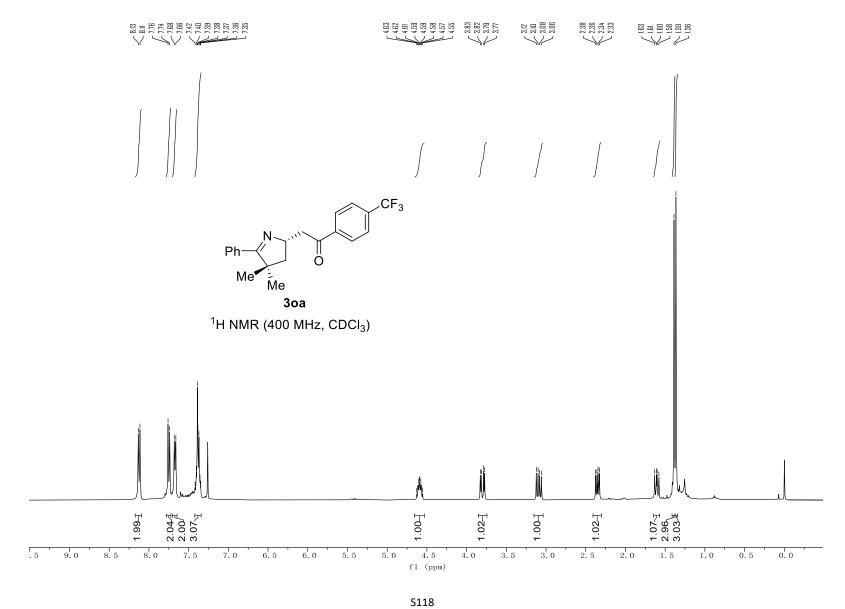


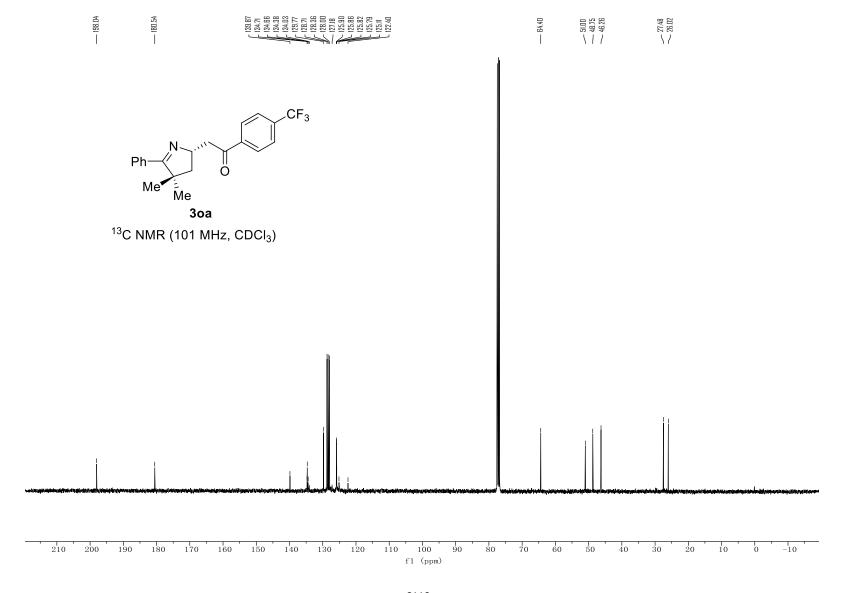




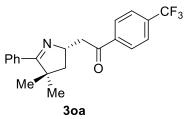




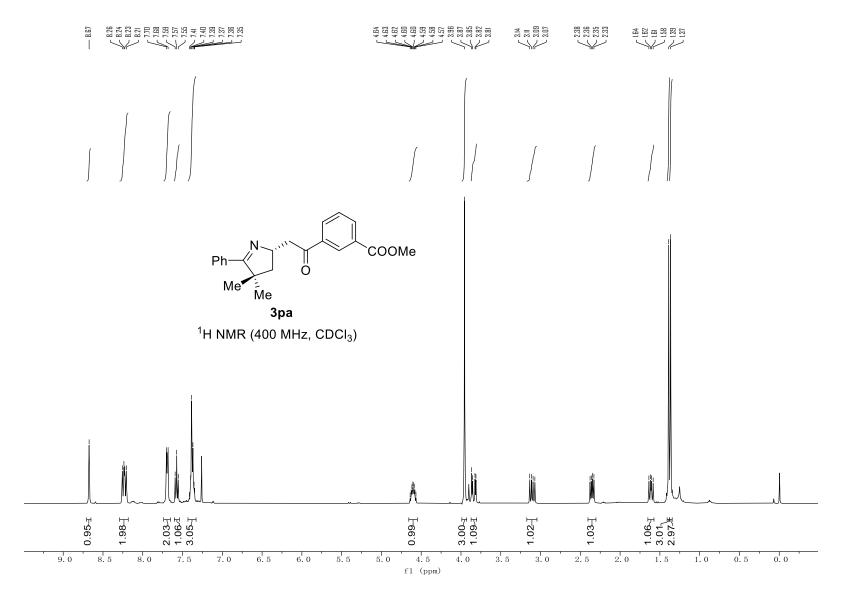


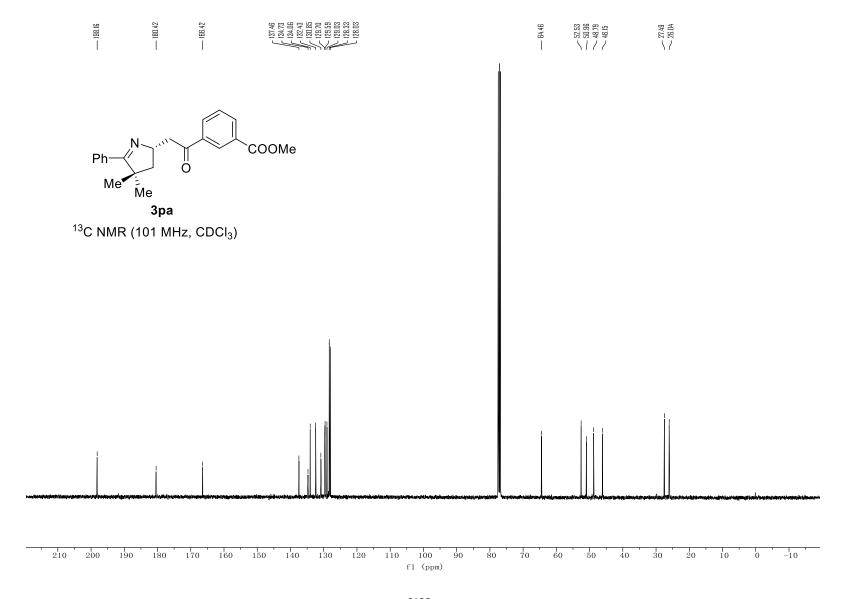


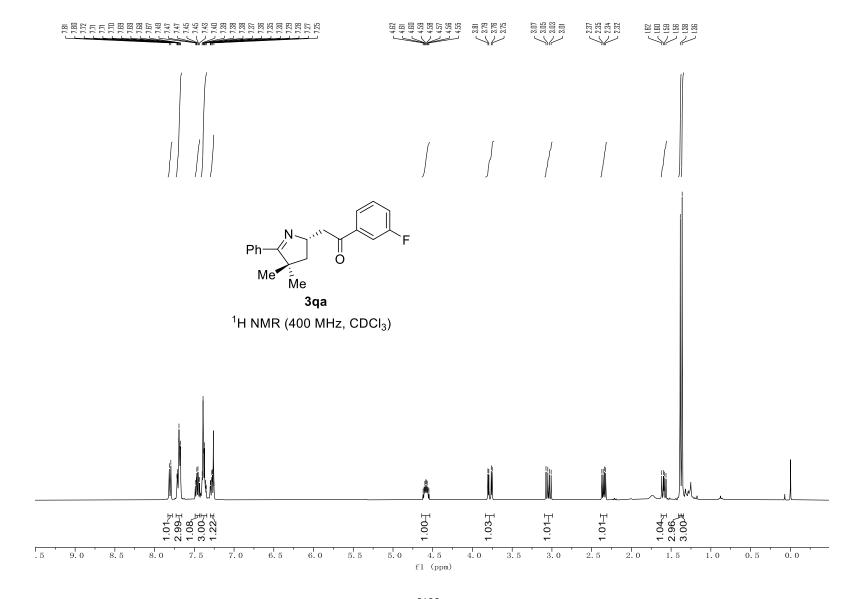


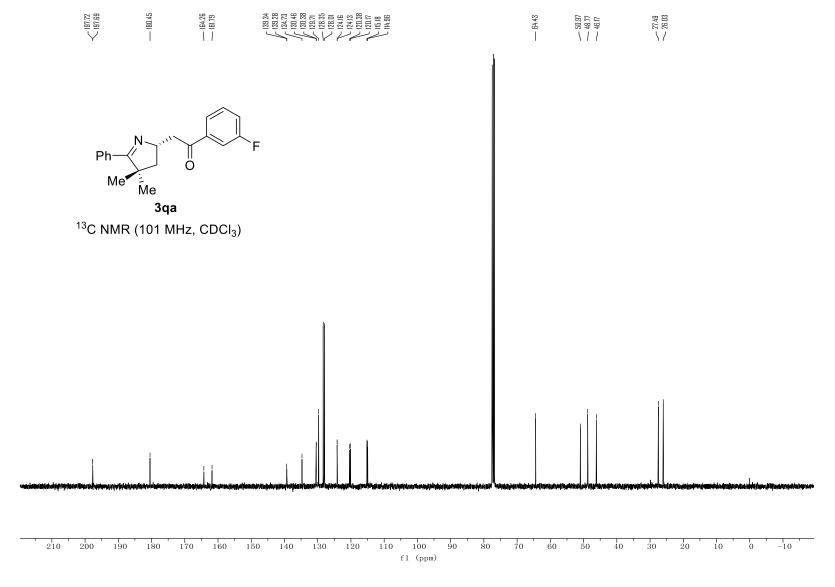


 19 F NMR (376 MHz, CDCl $_3$)

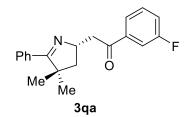




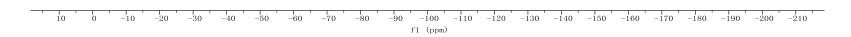


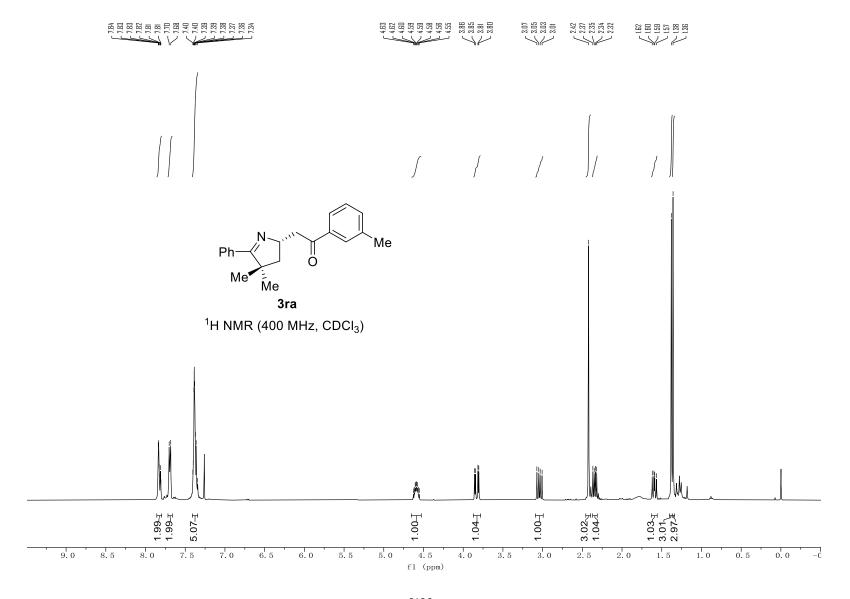


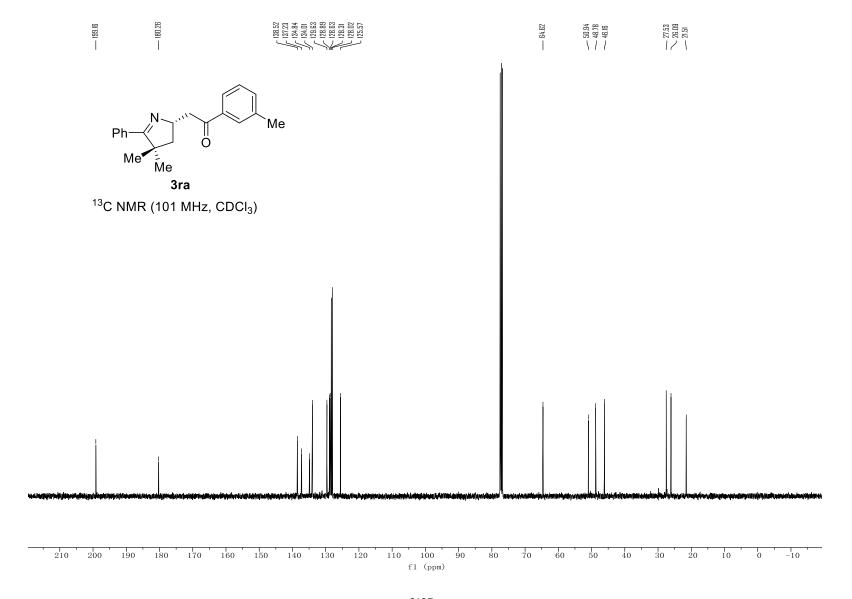


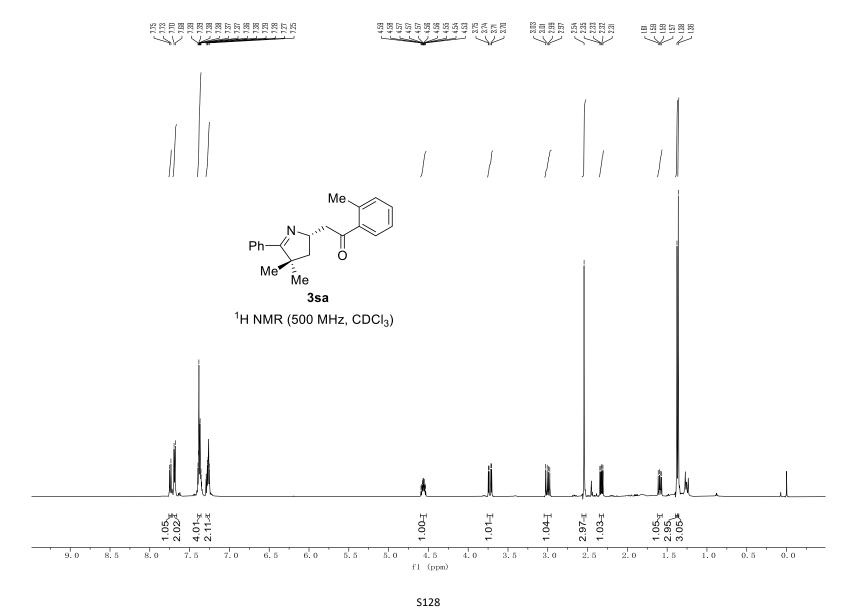


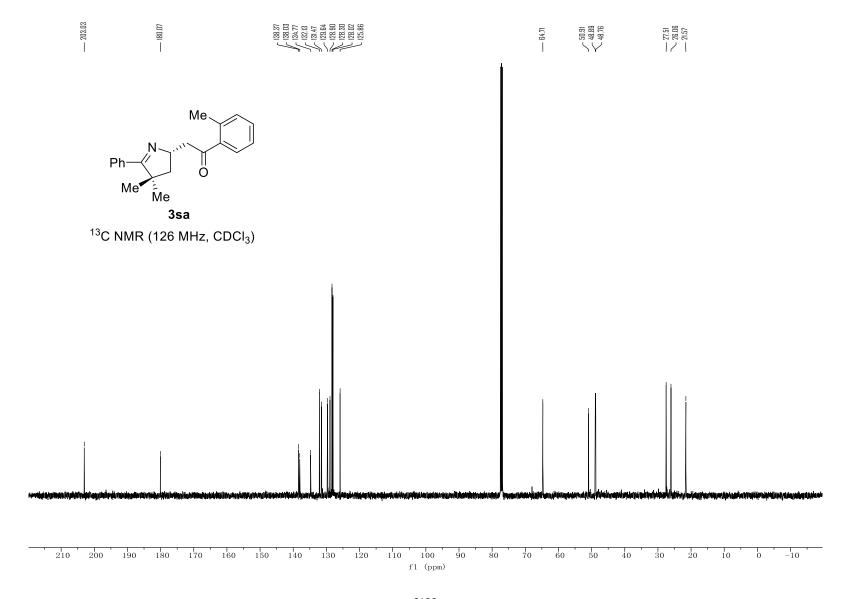
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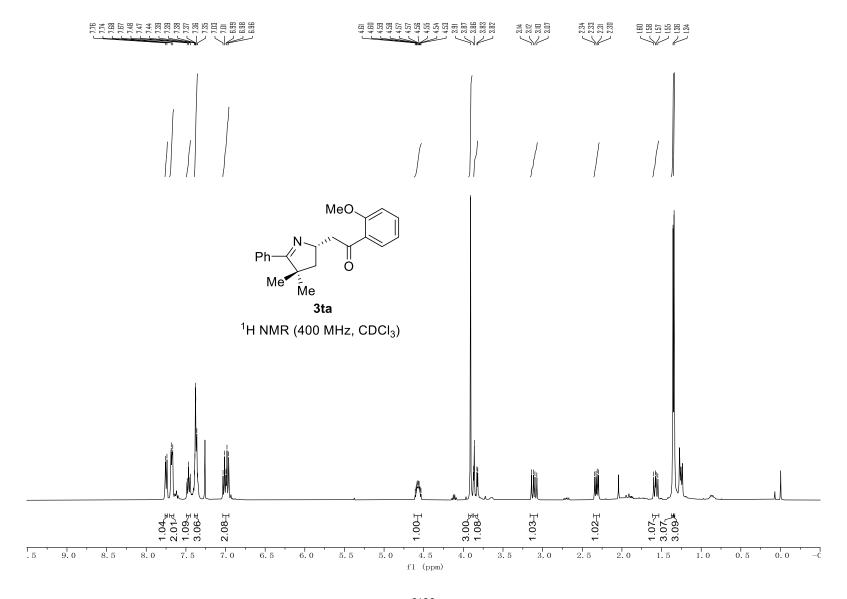


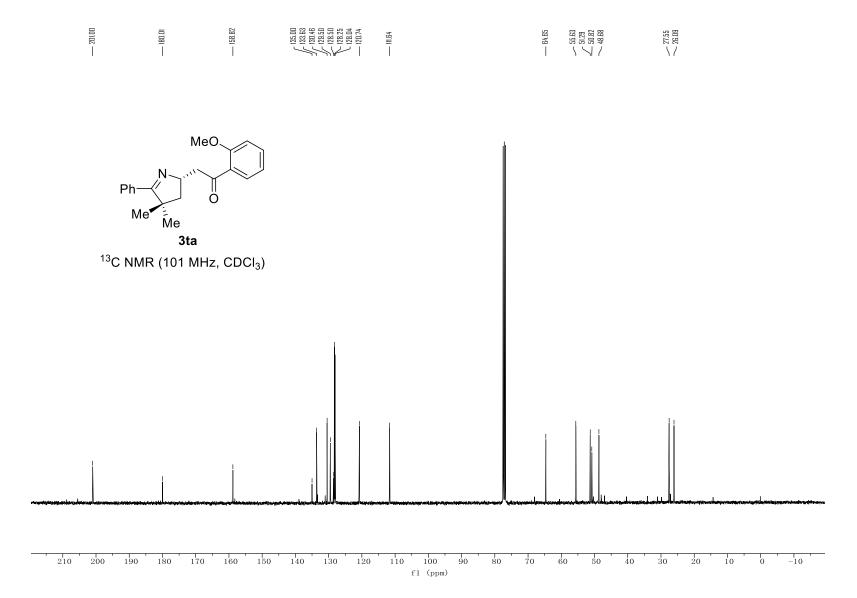


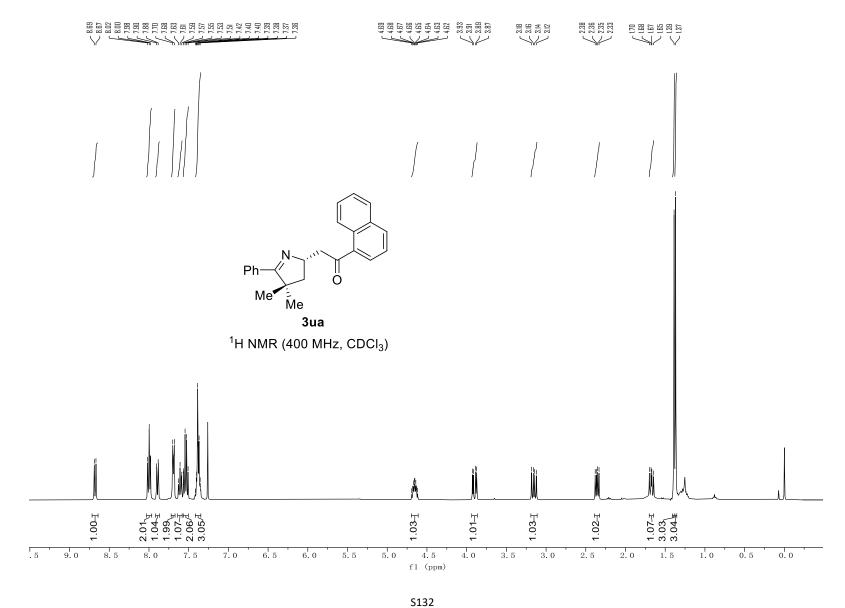


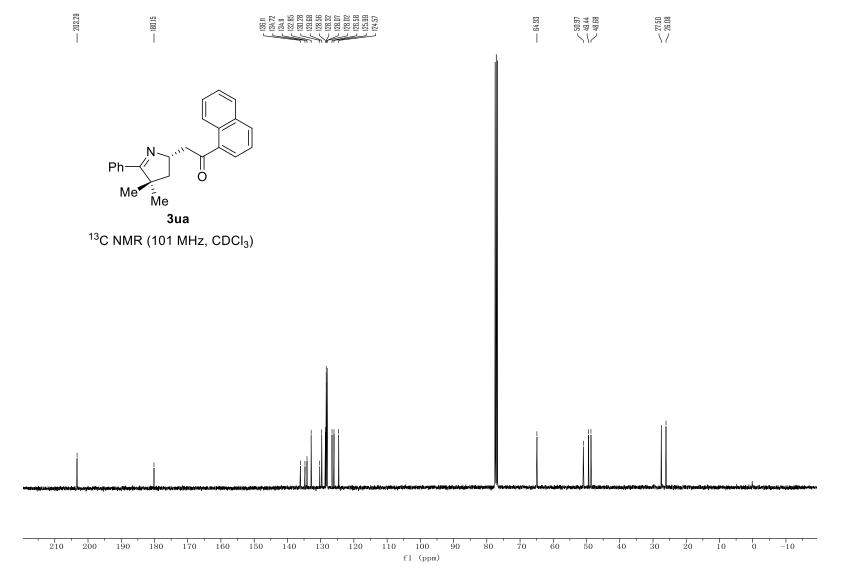


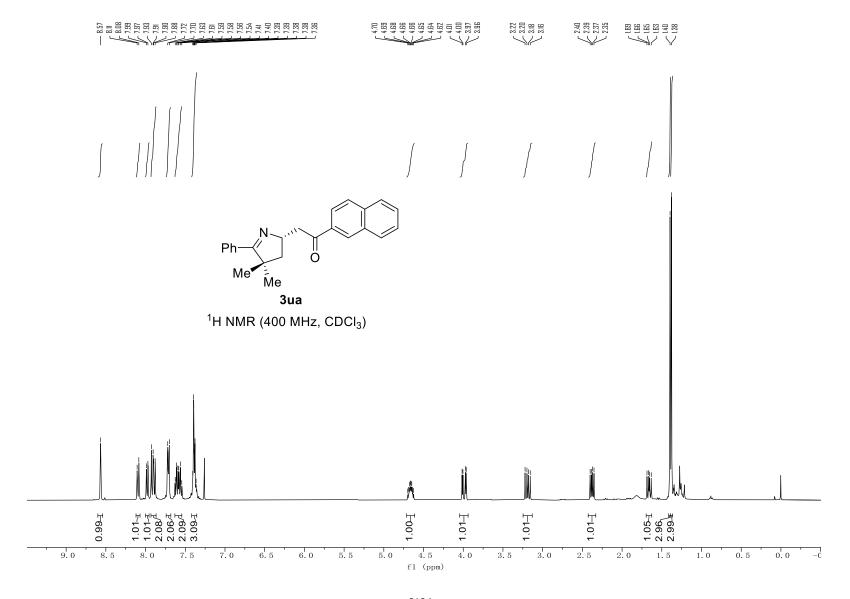


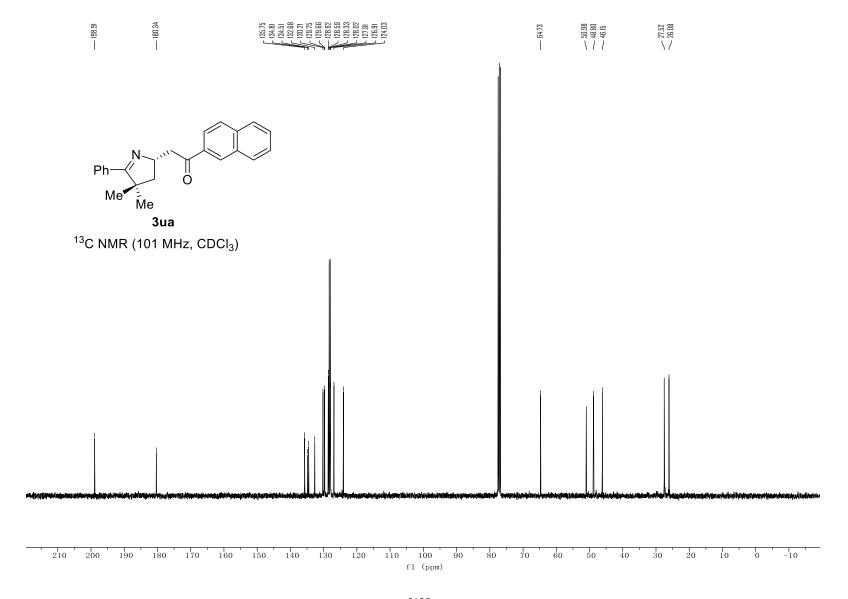


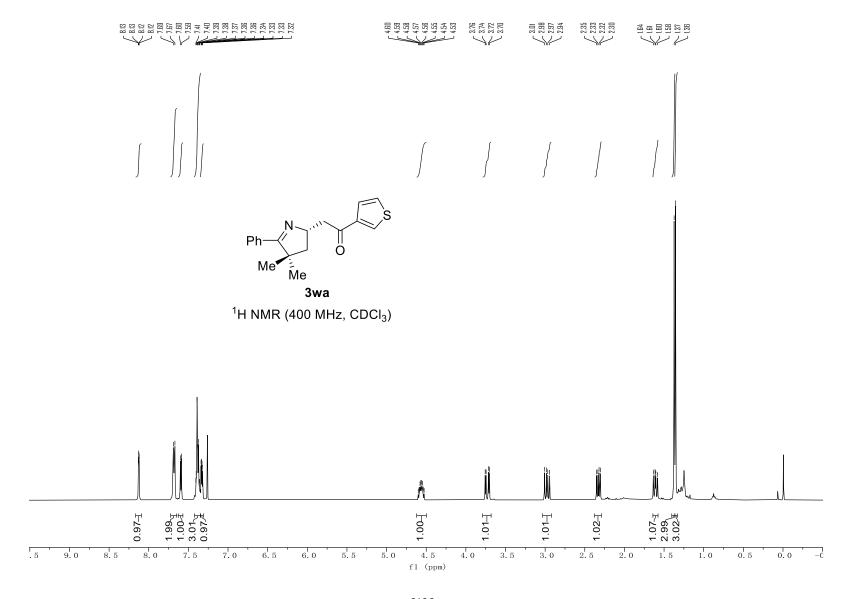


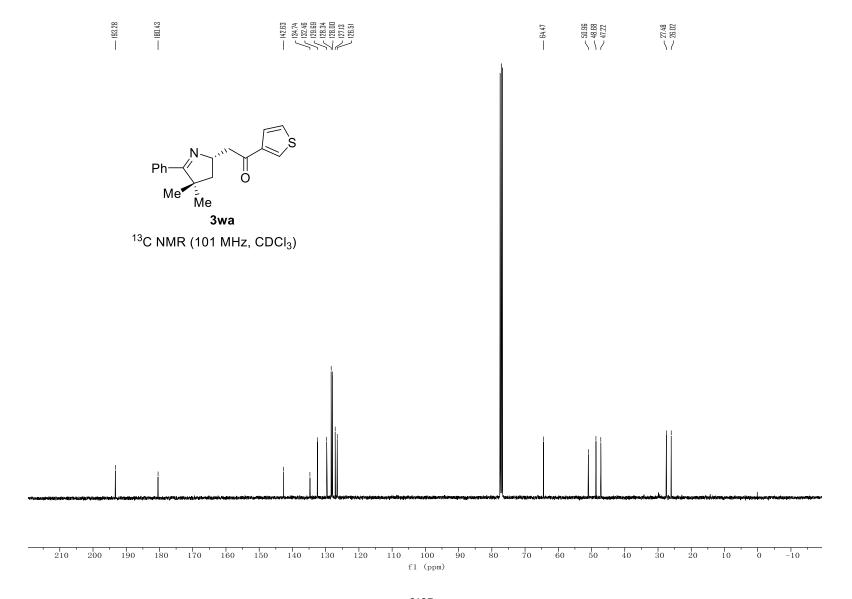


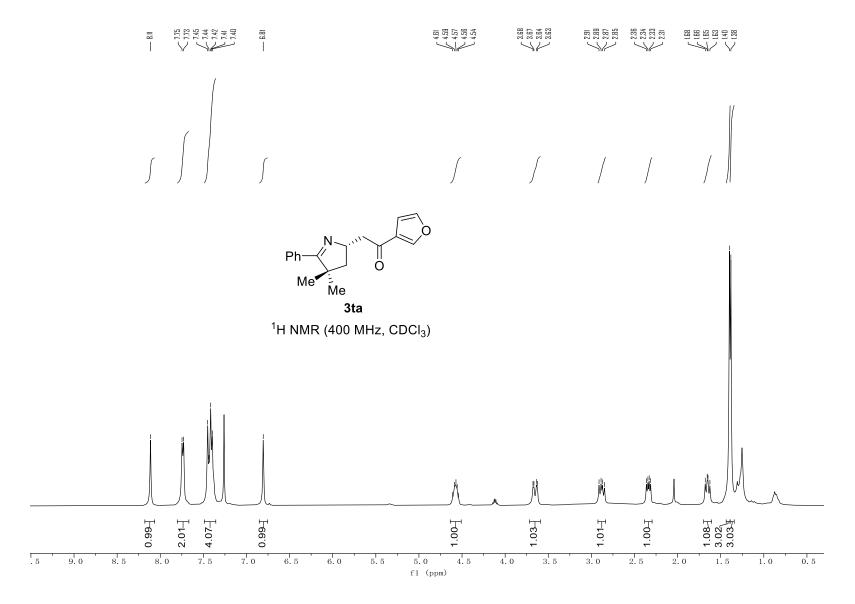


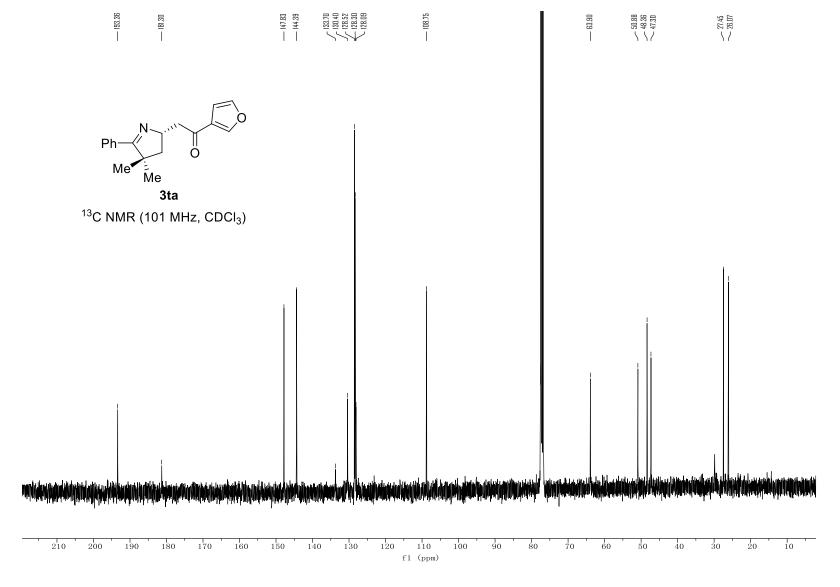


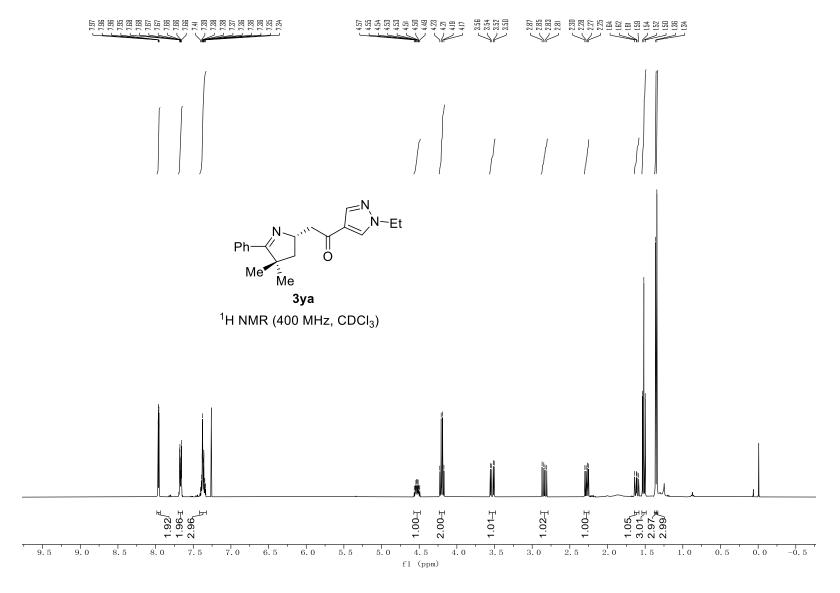


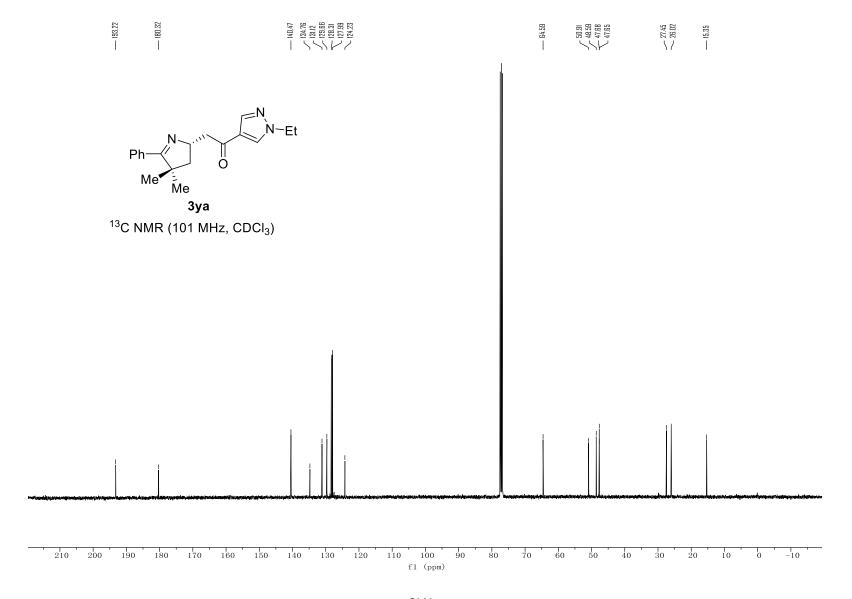


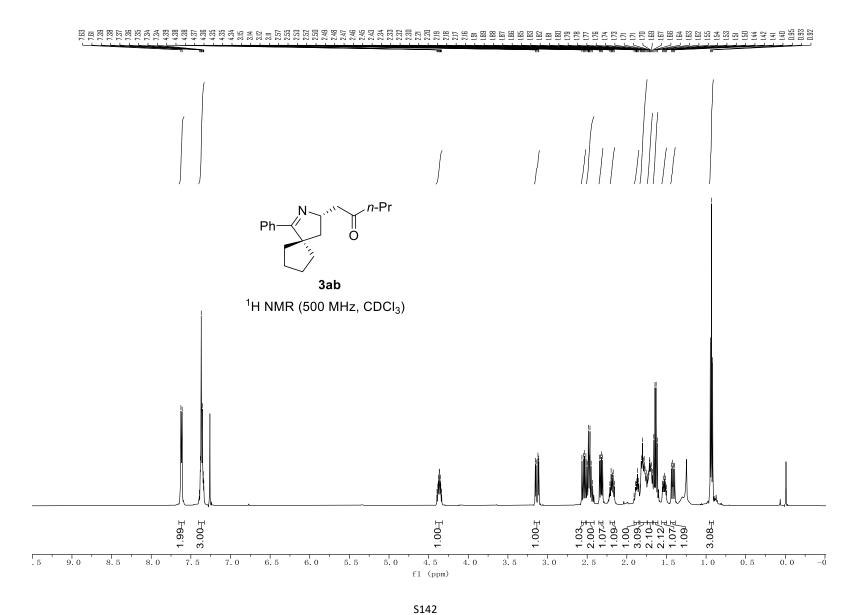


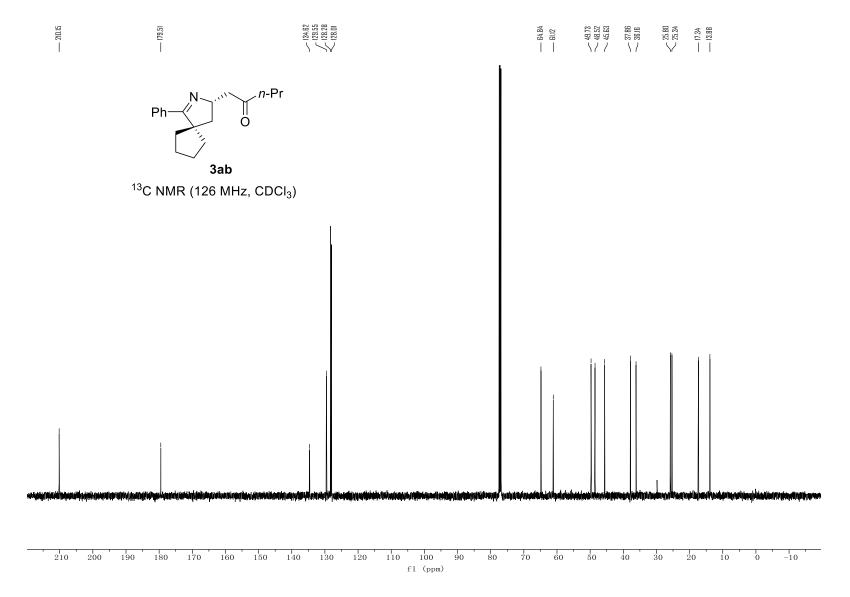


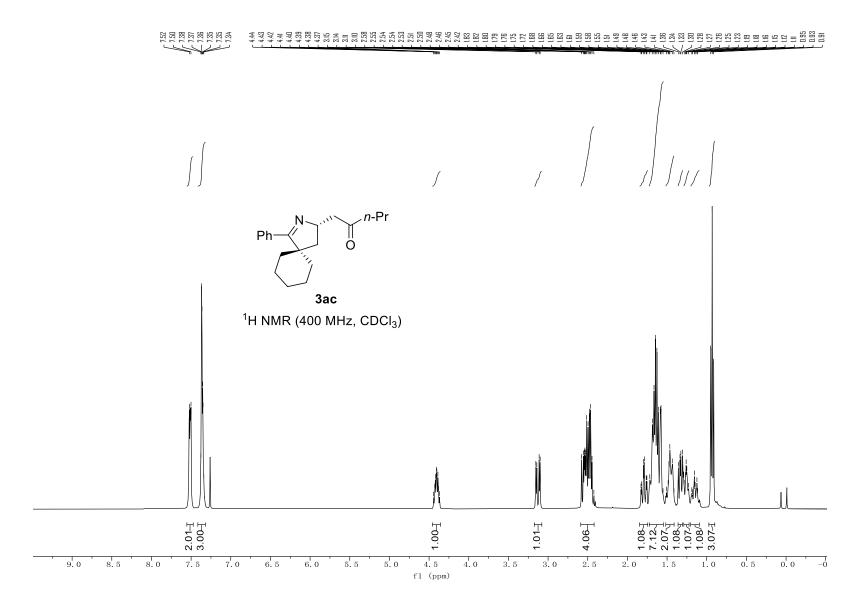


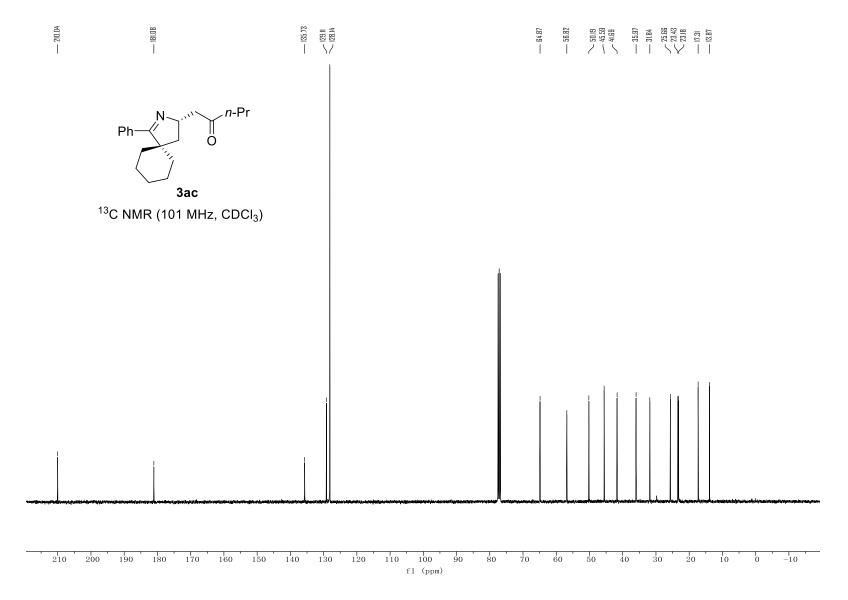


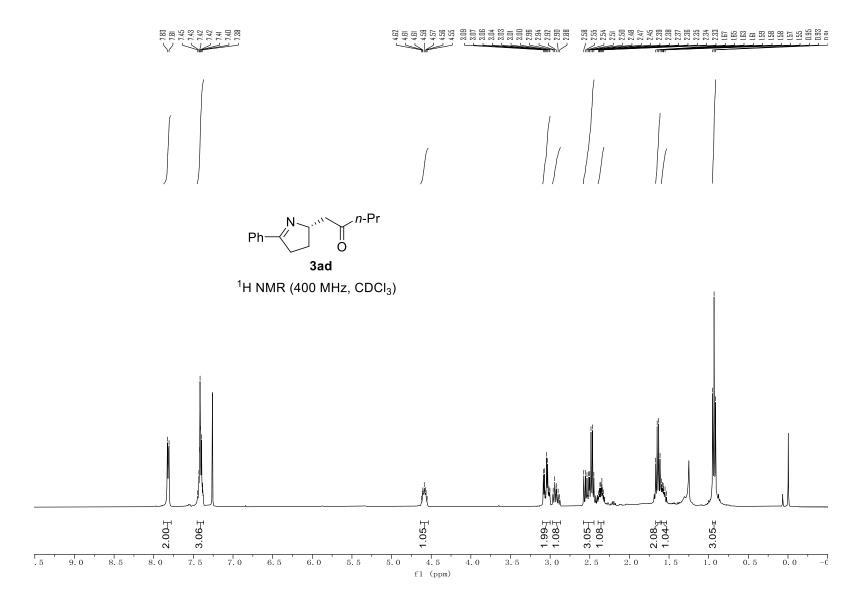


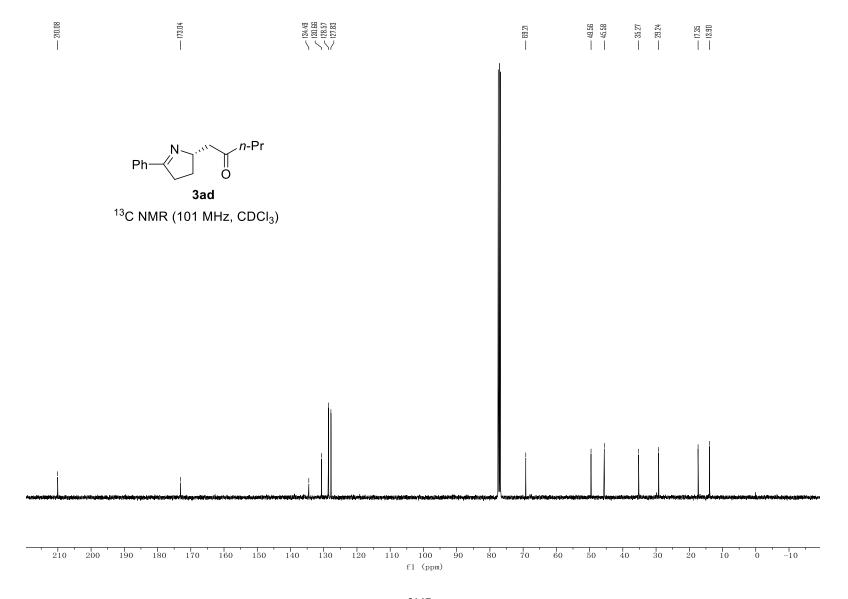


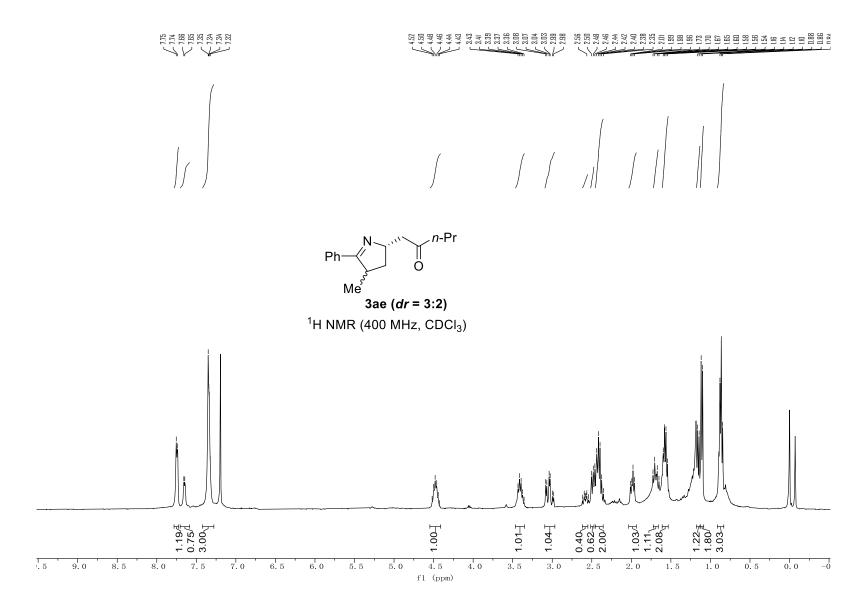


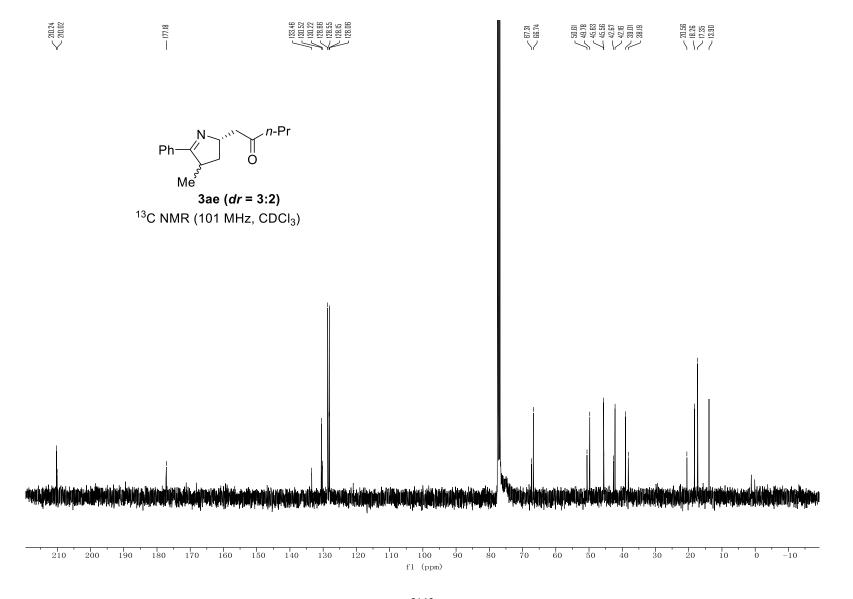


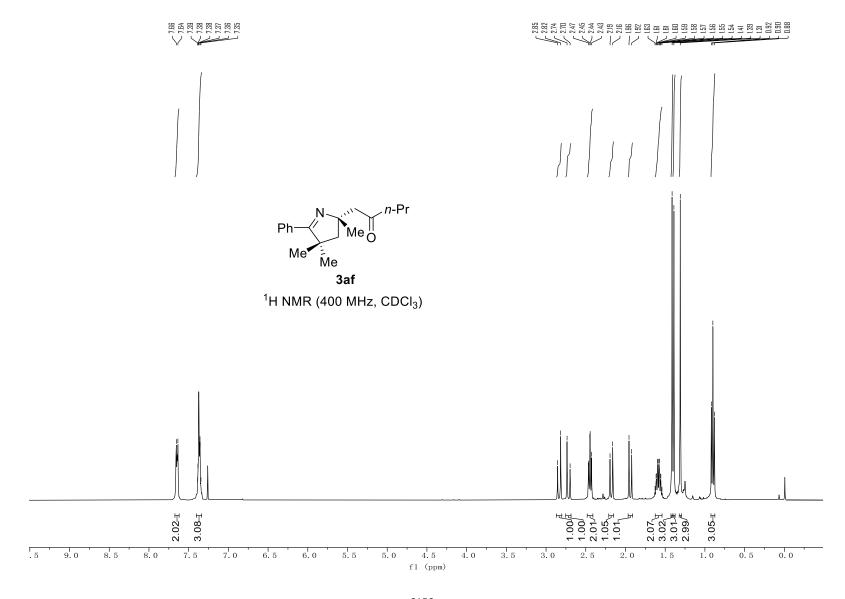


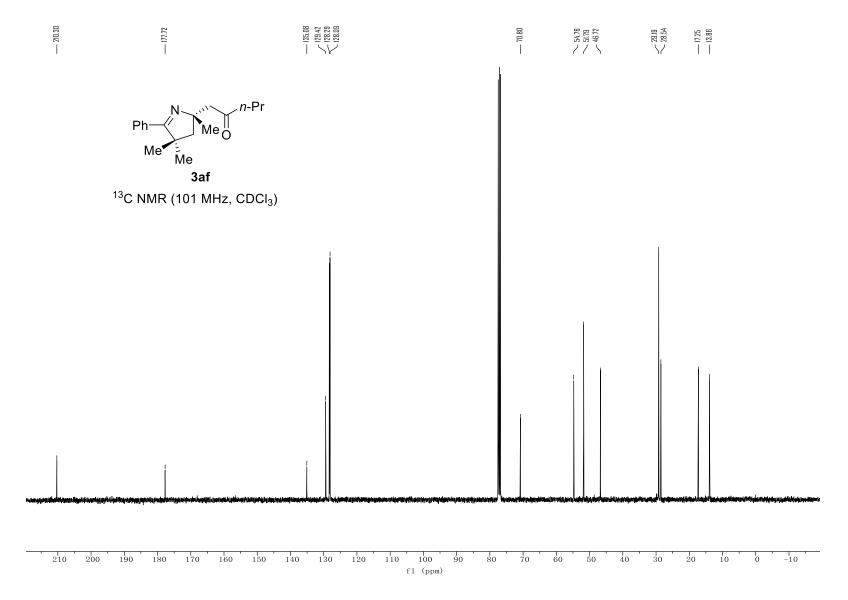


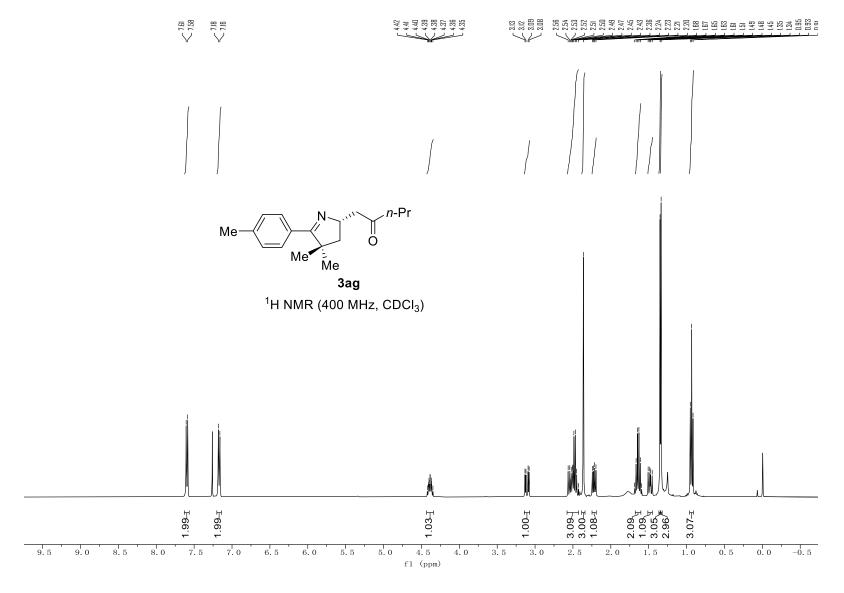


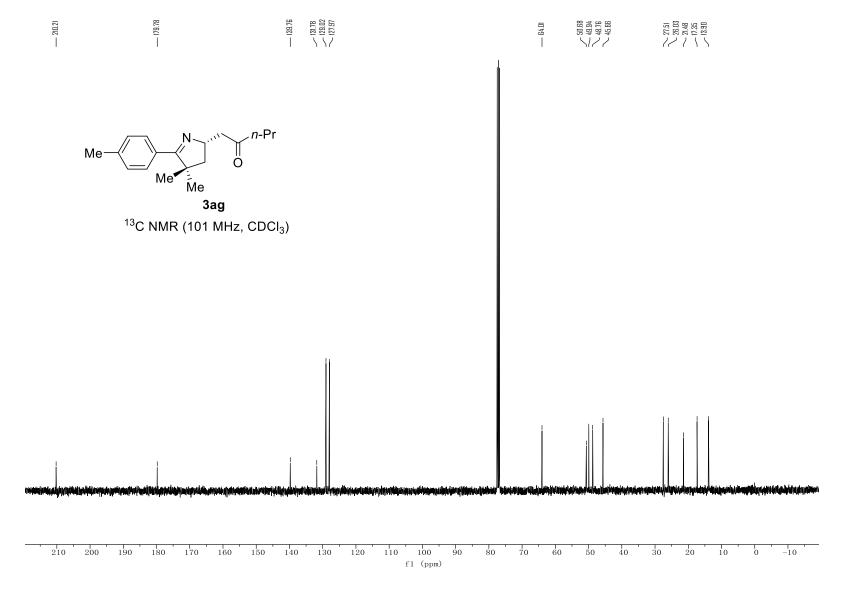


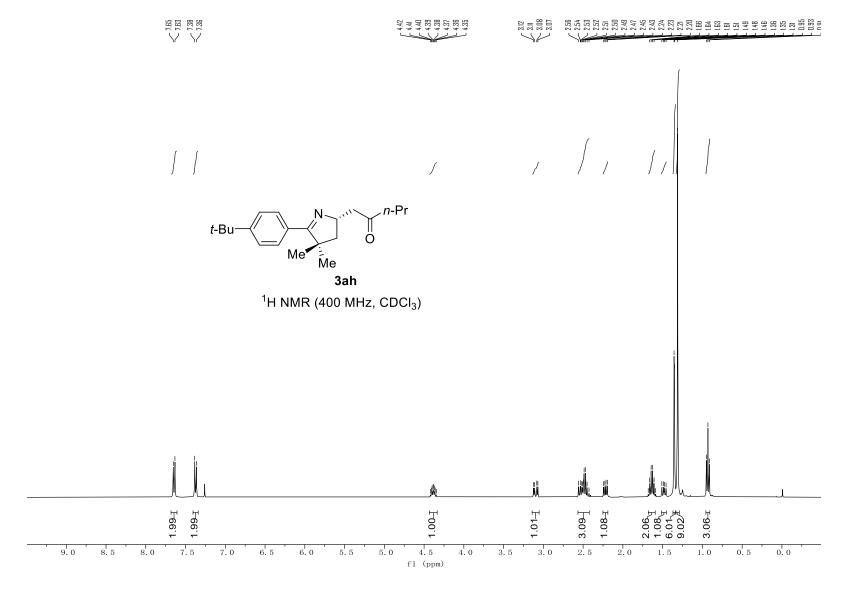


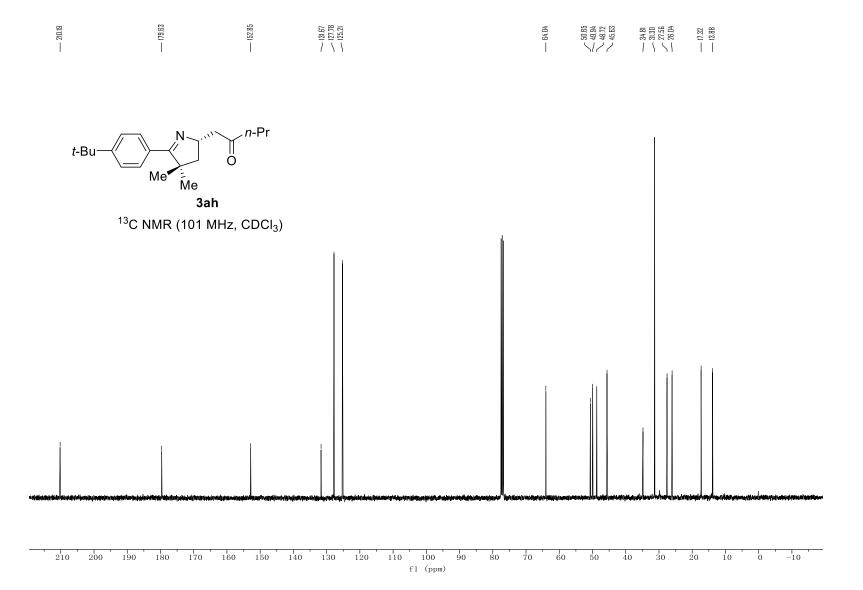


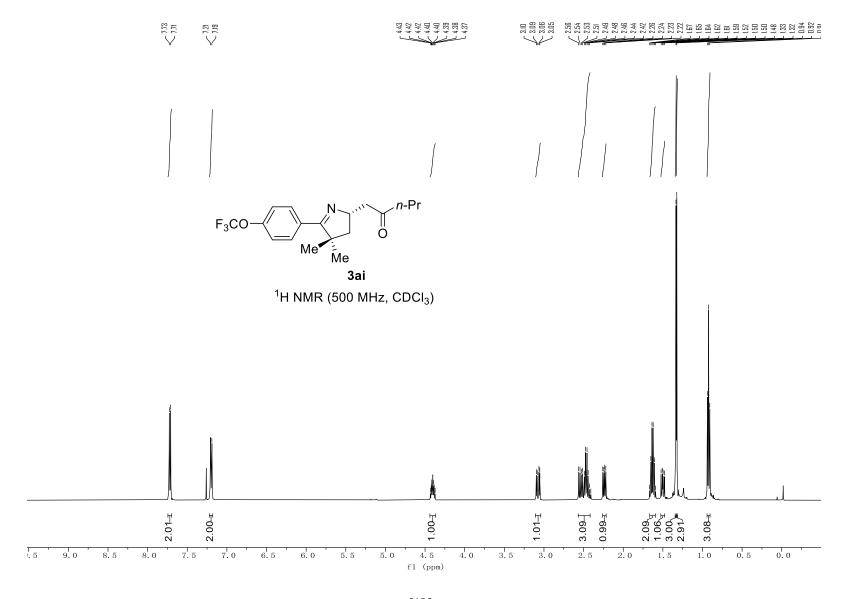


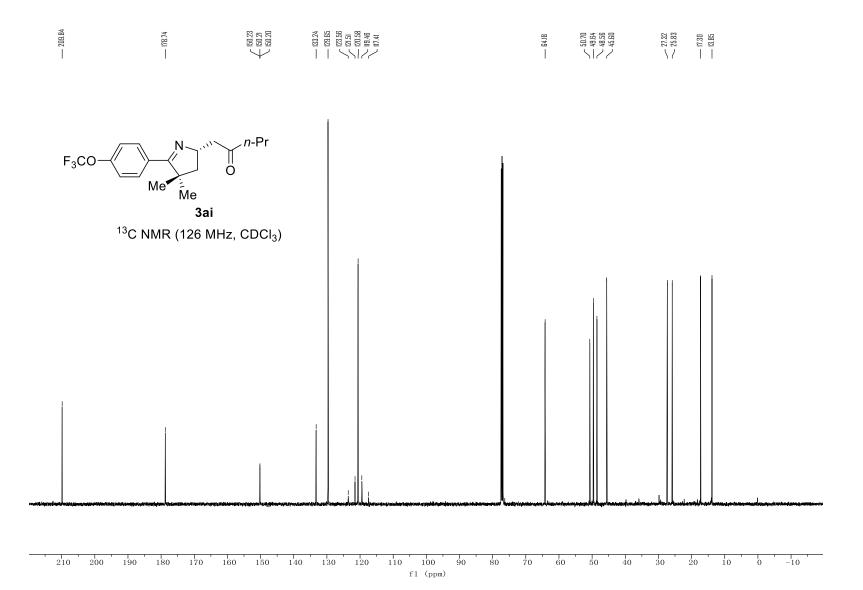


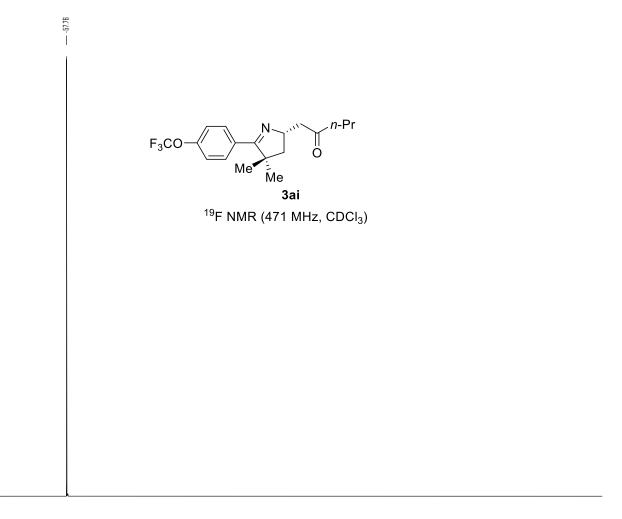


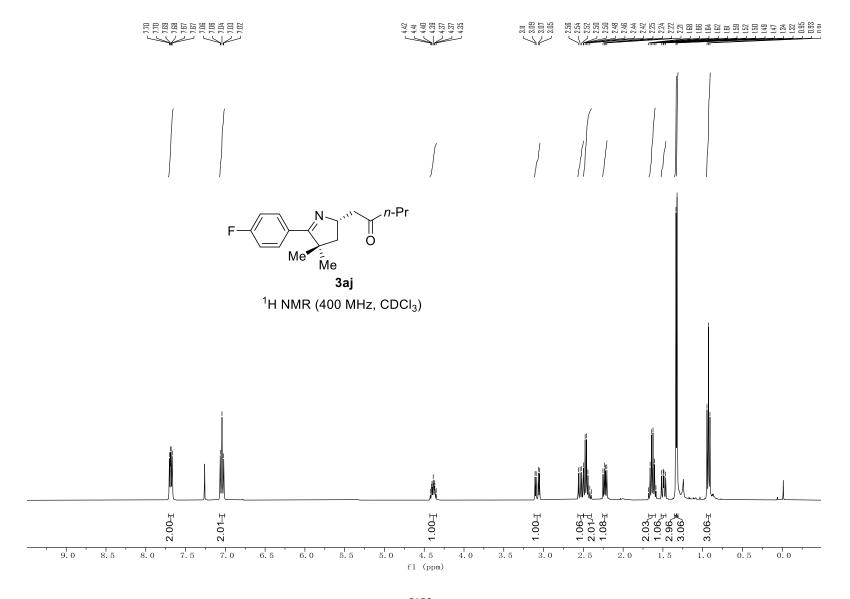


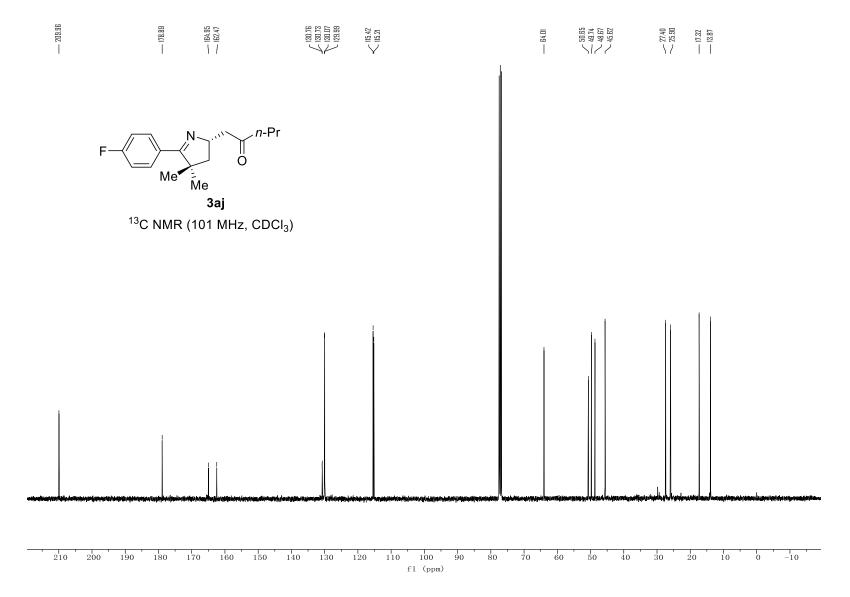


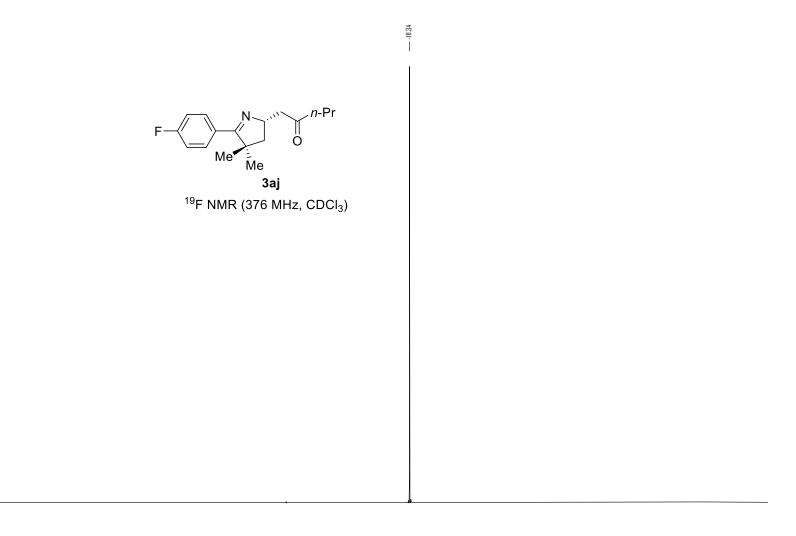




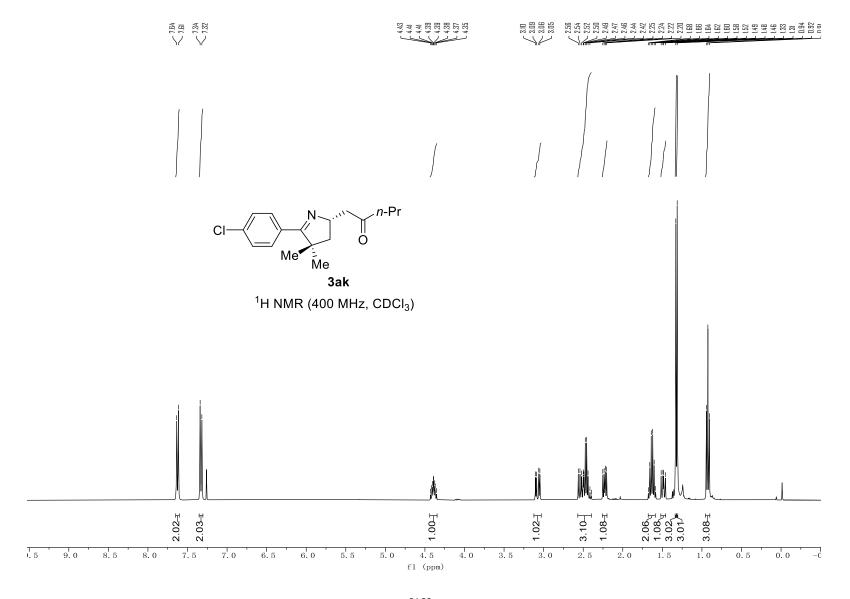


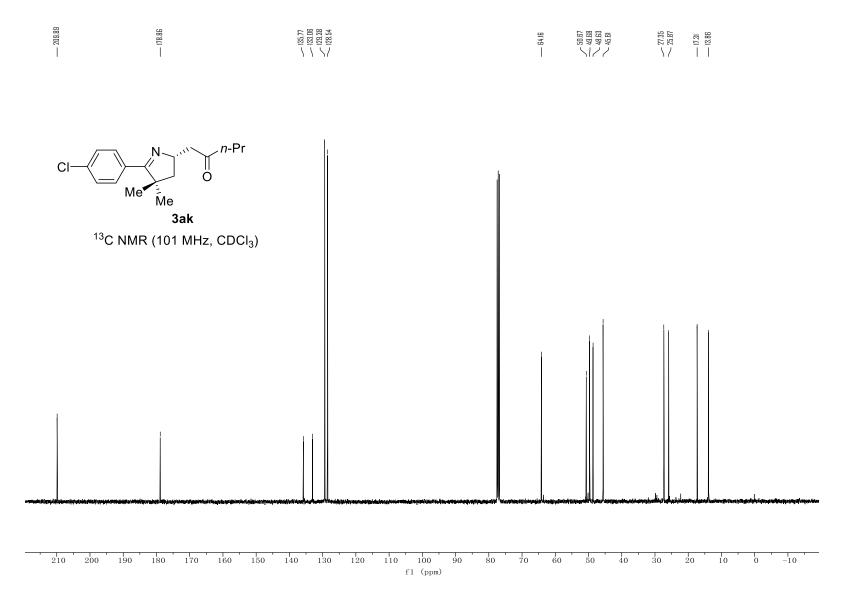


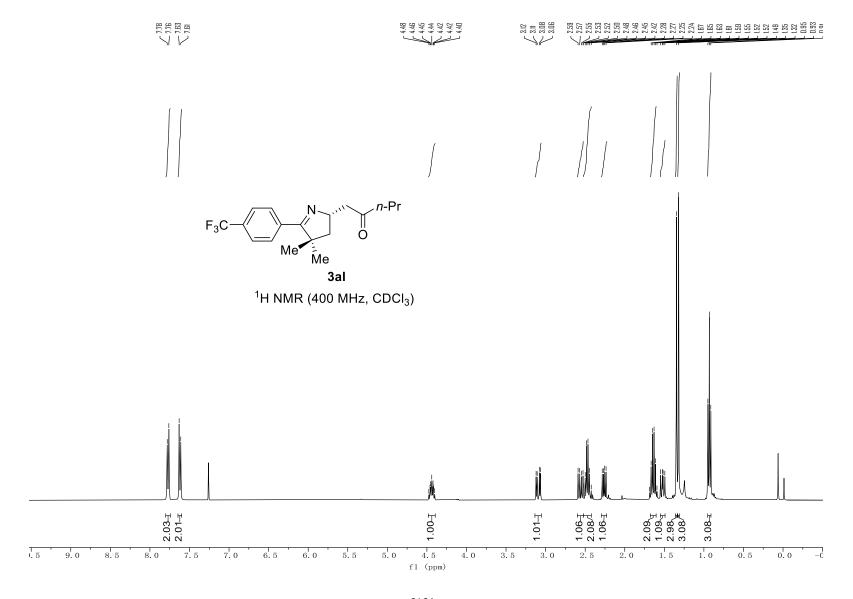


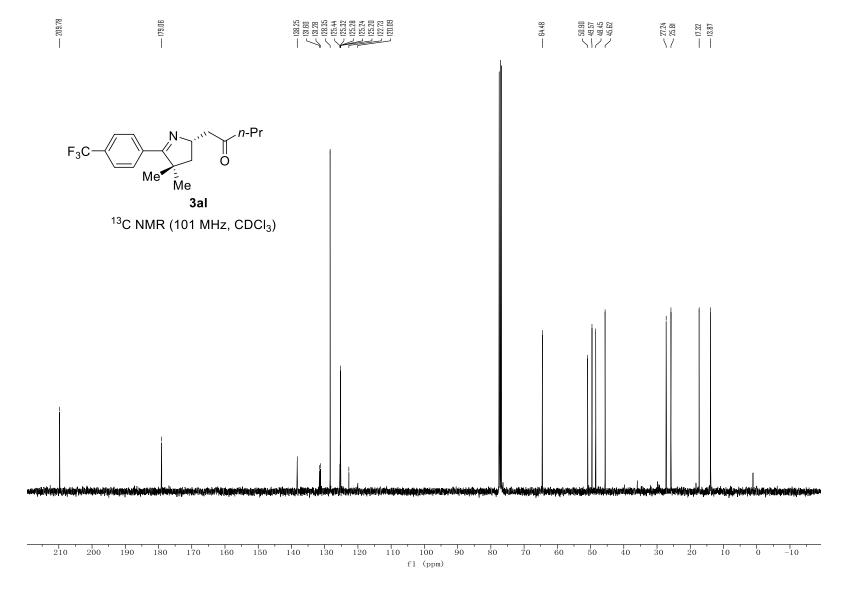


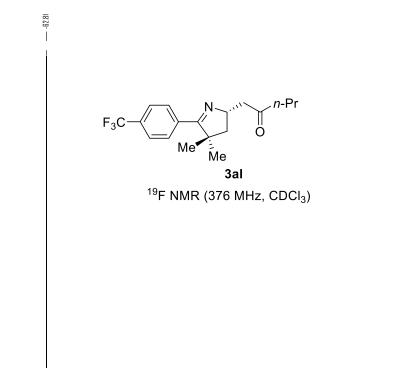
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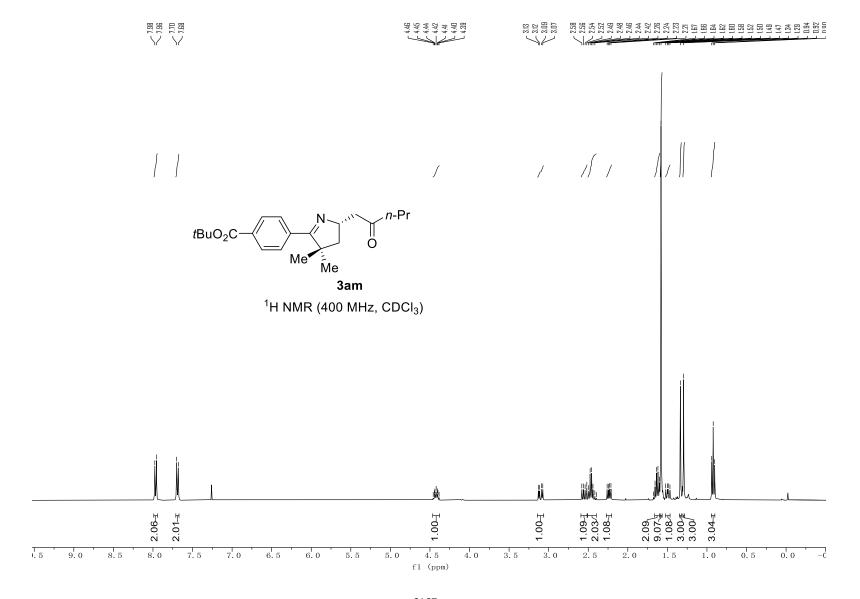


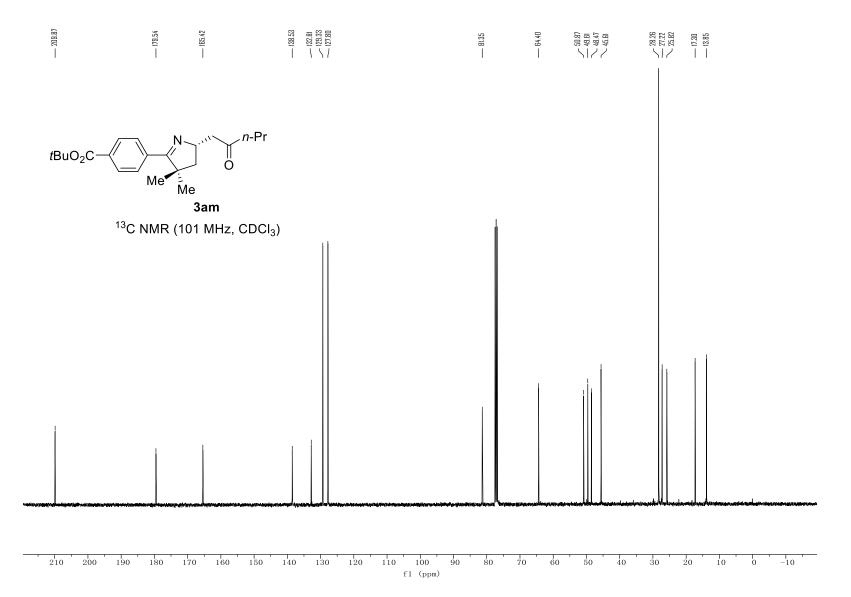


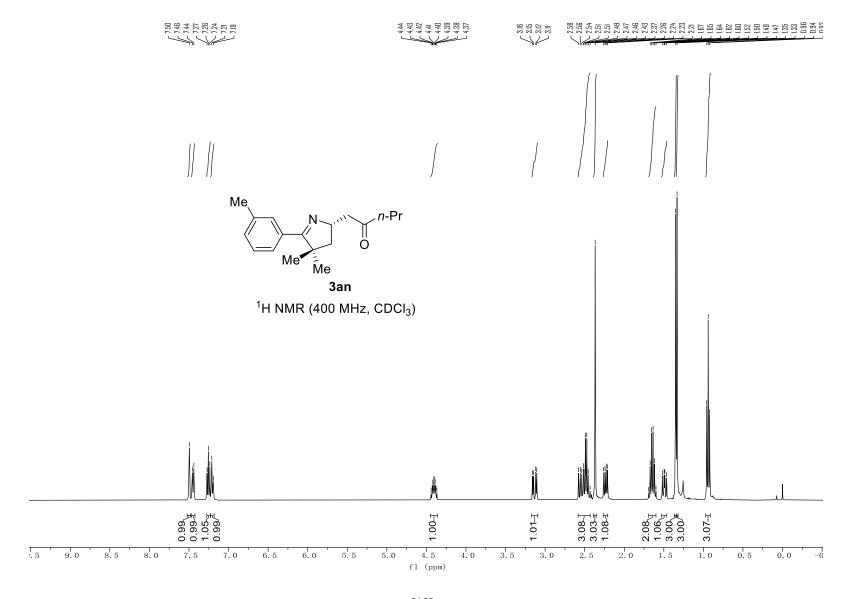


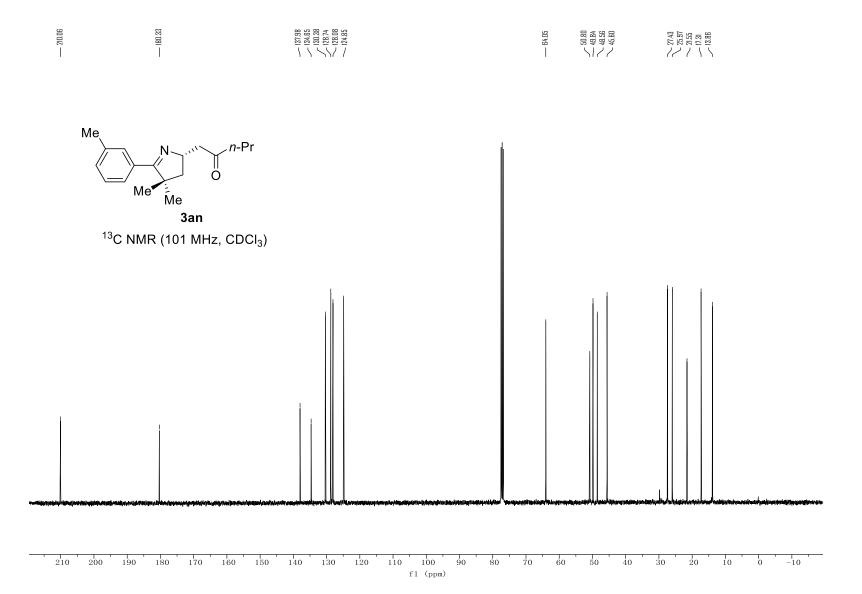


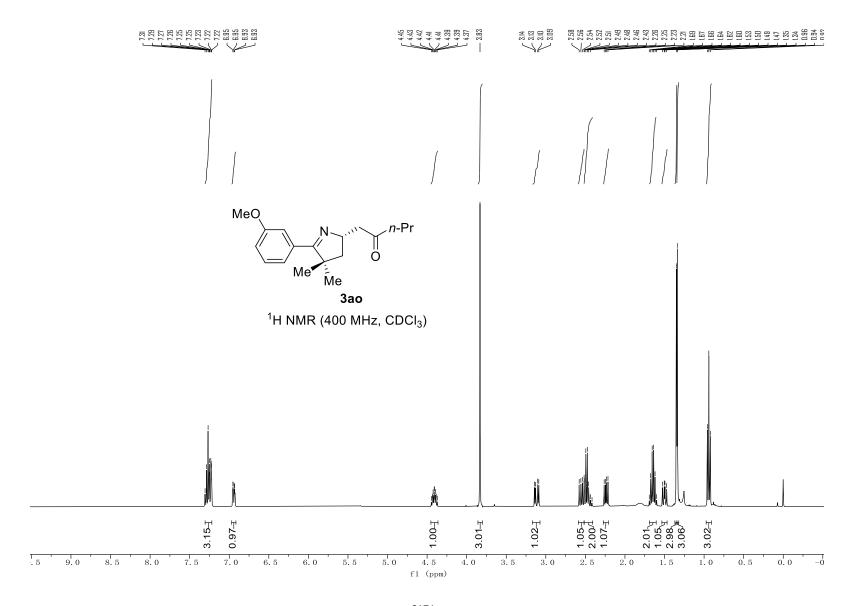


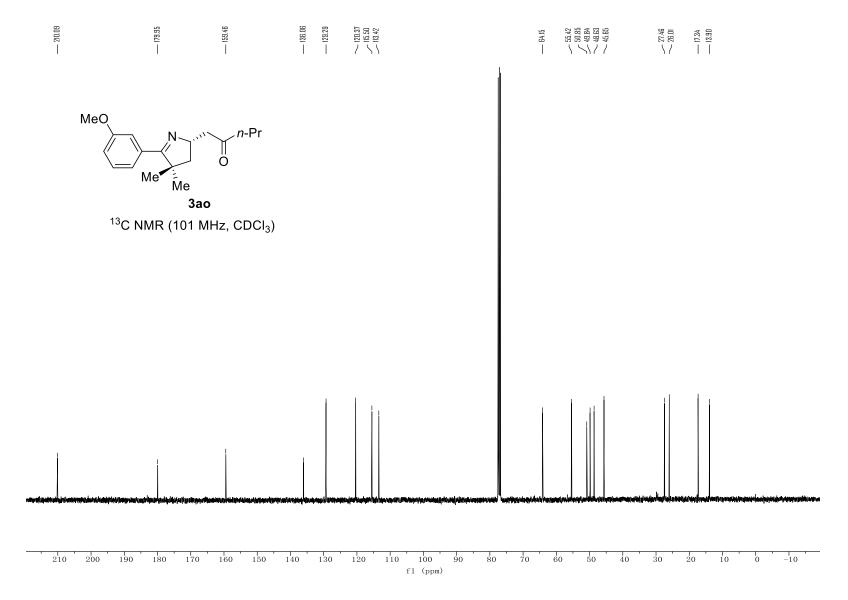


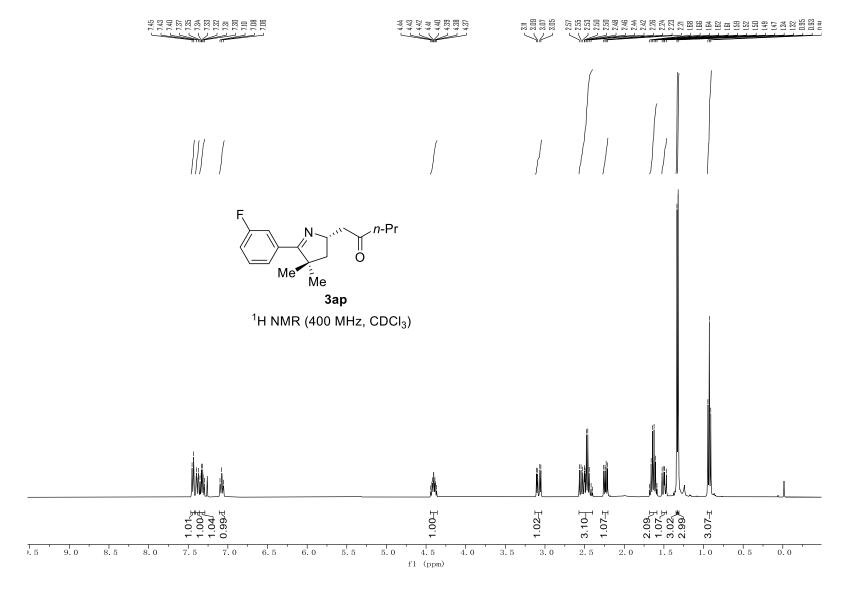


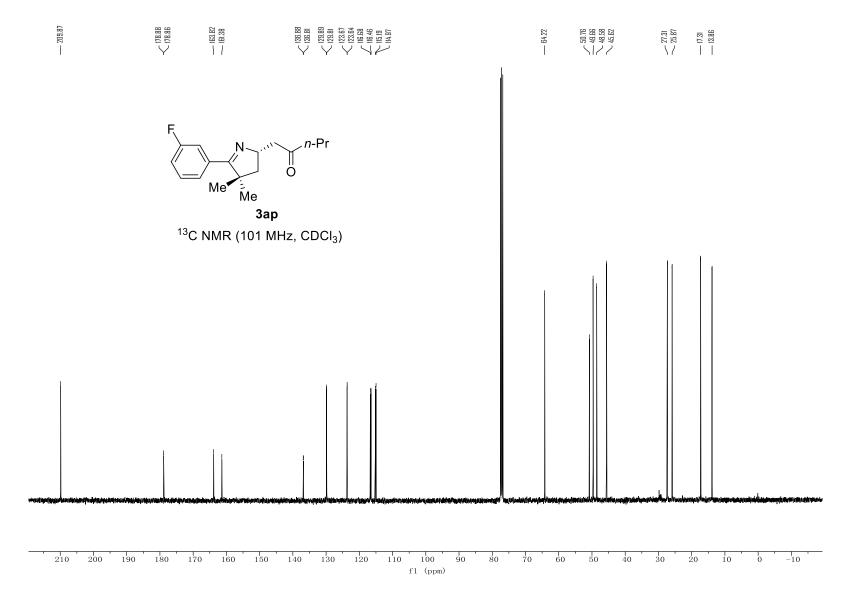


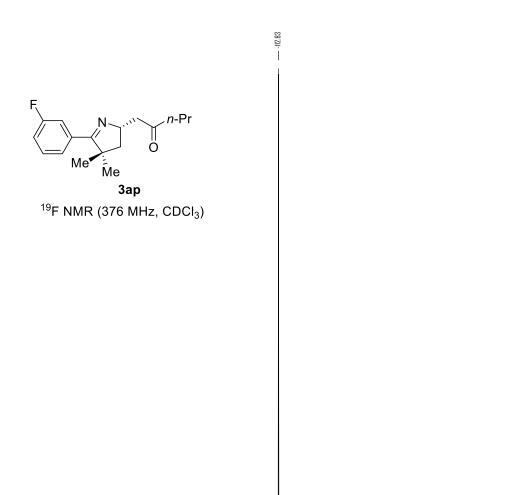


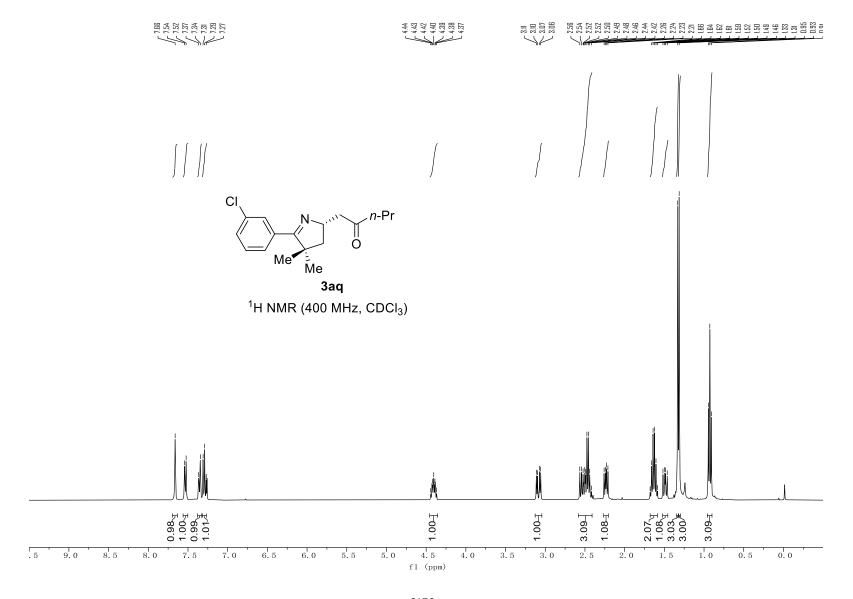


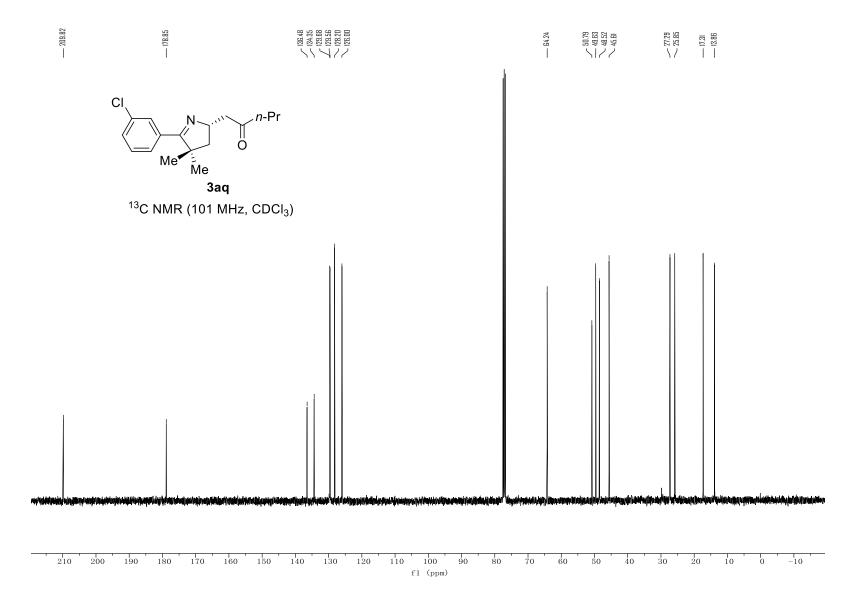


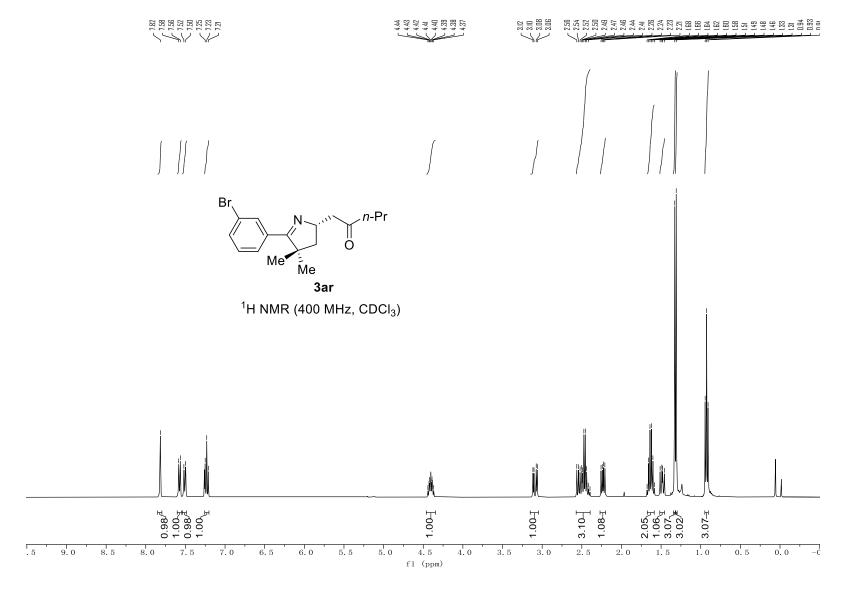


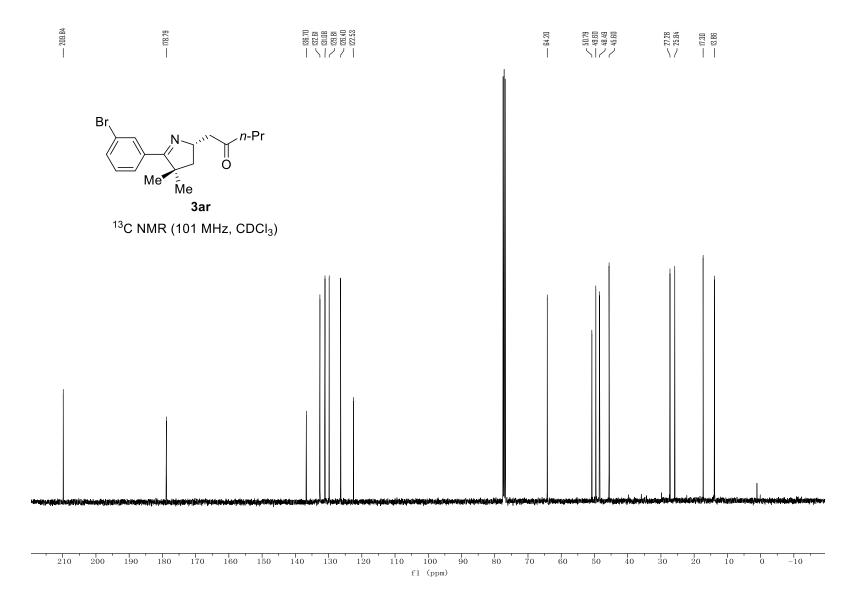


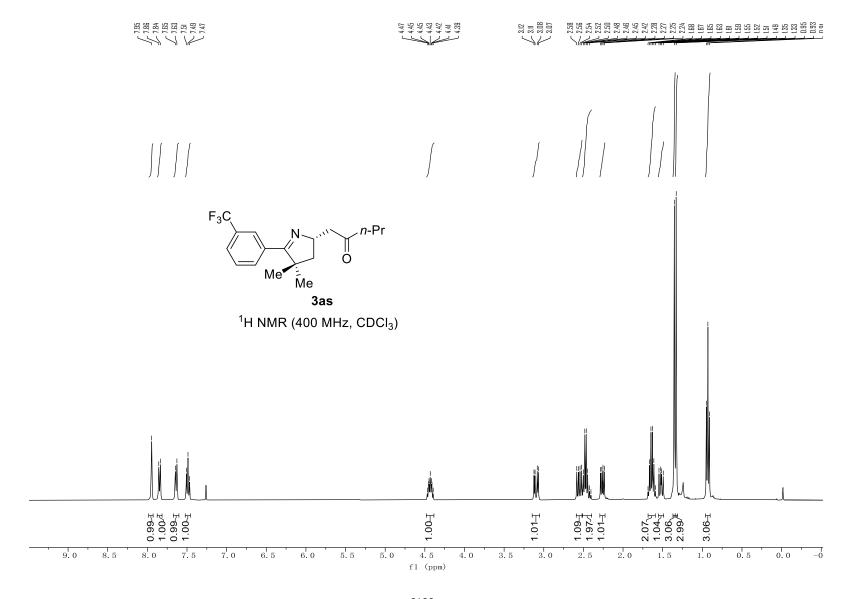


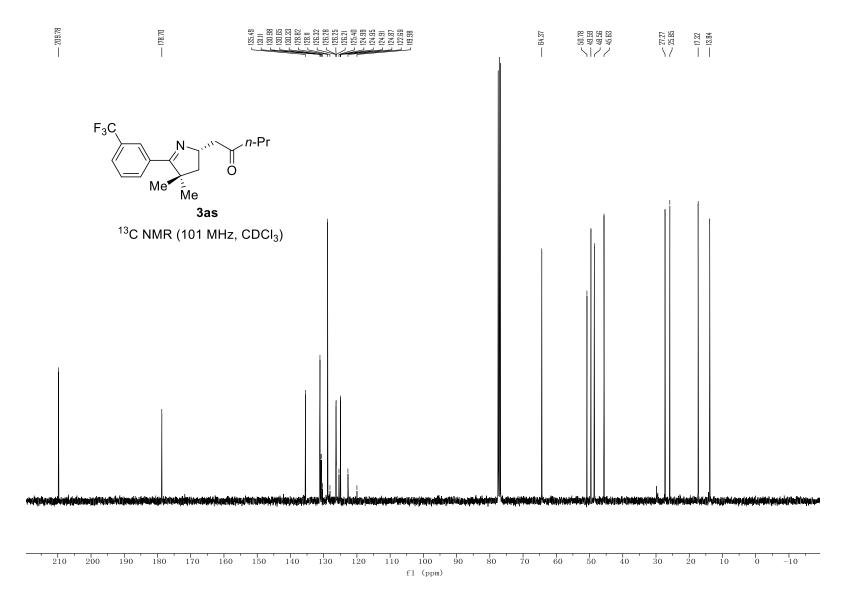


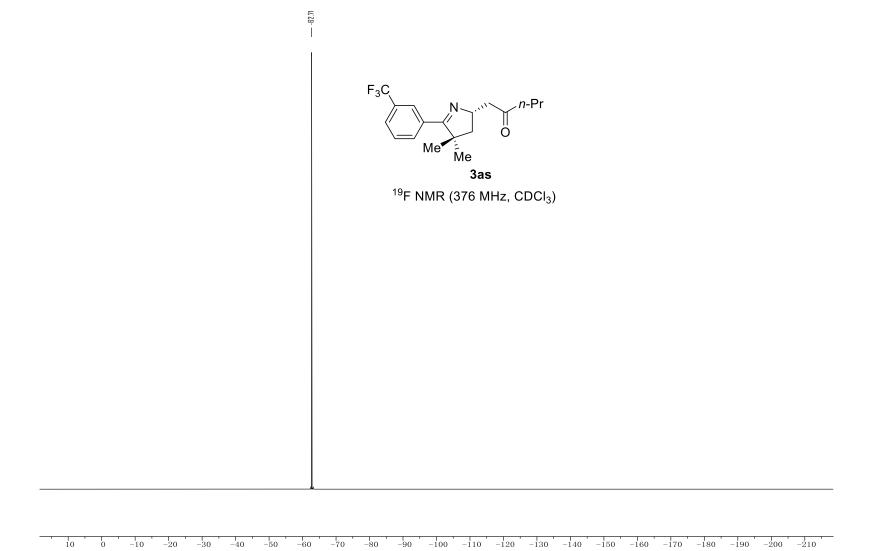




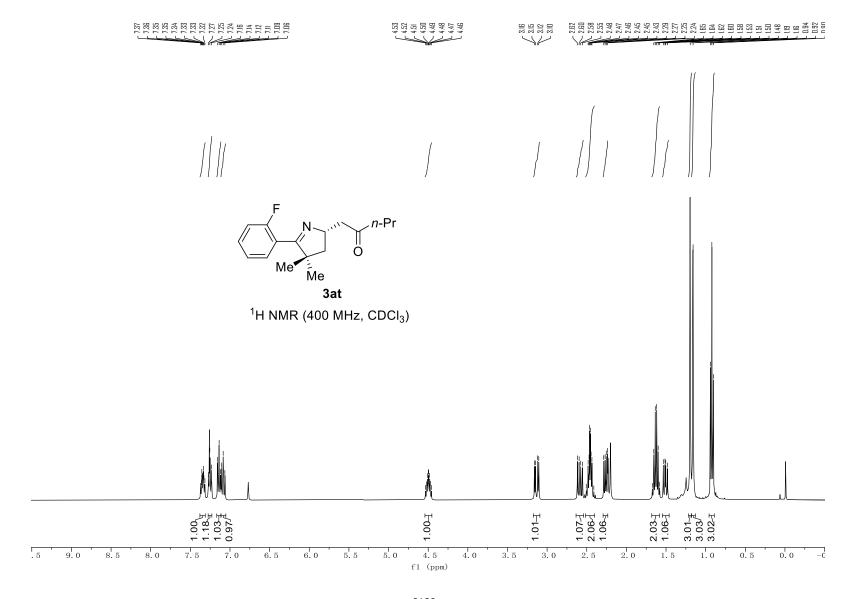


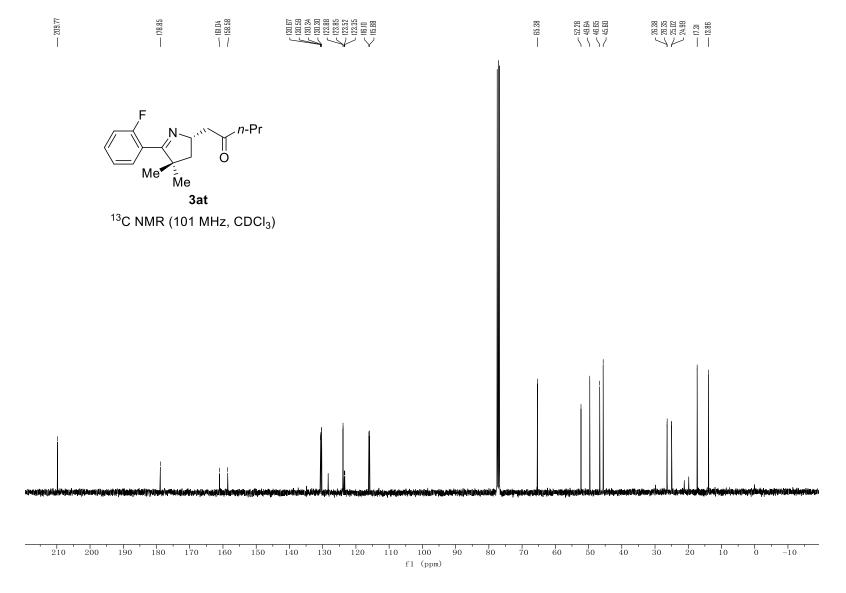


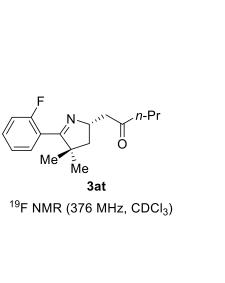


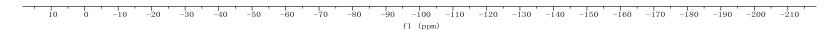


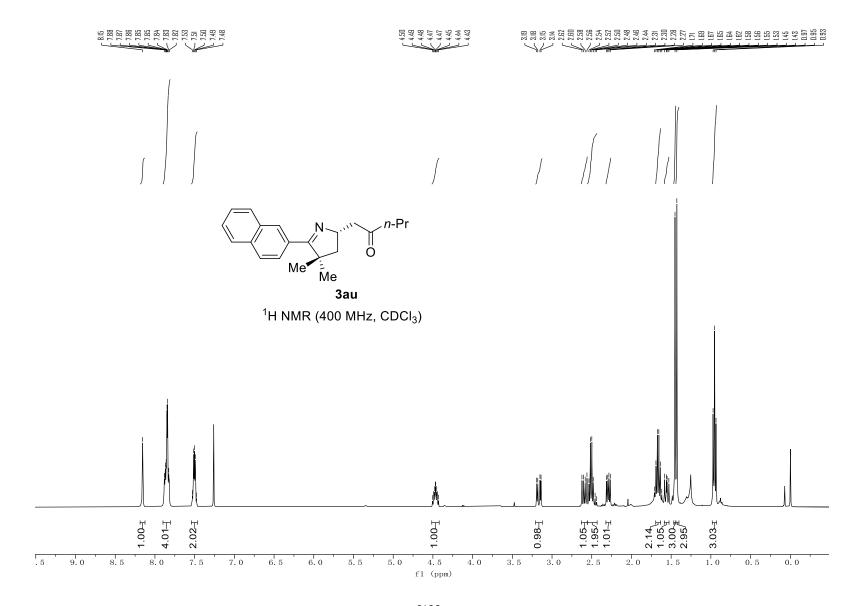
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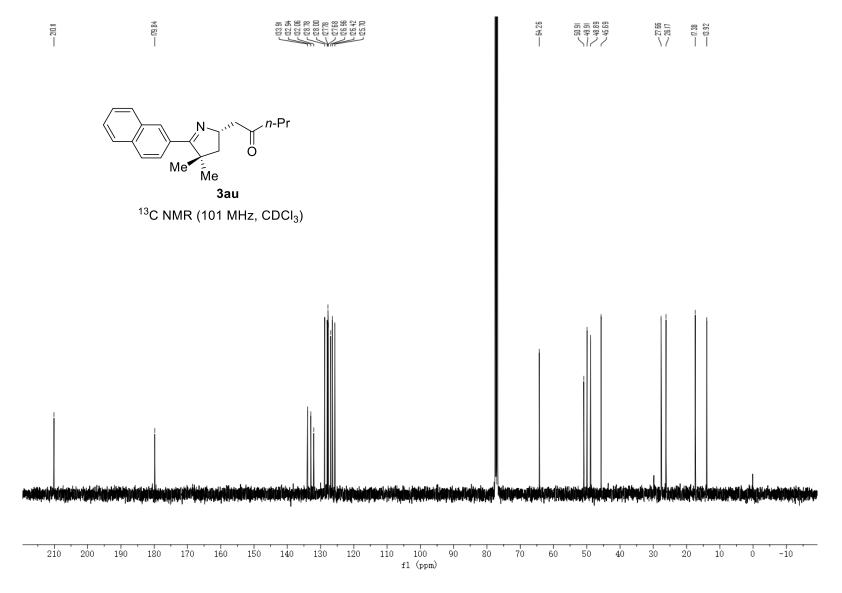


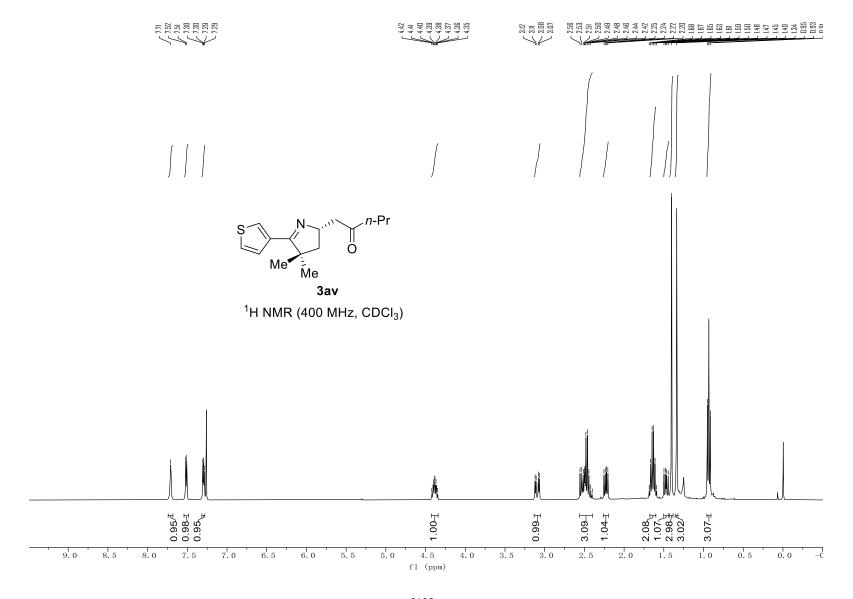


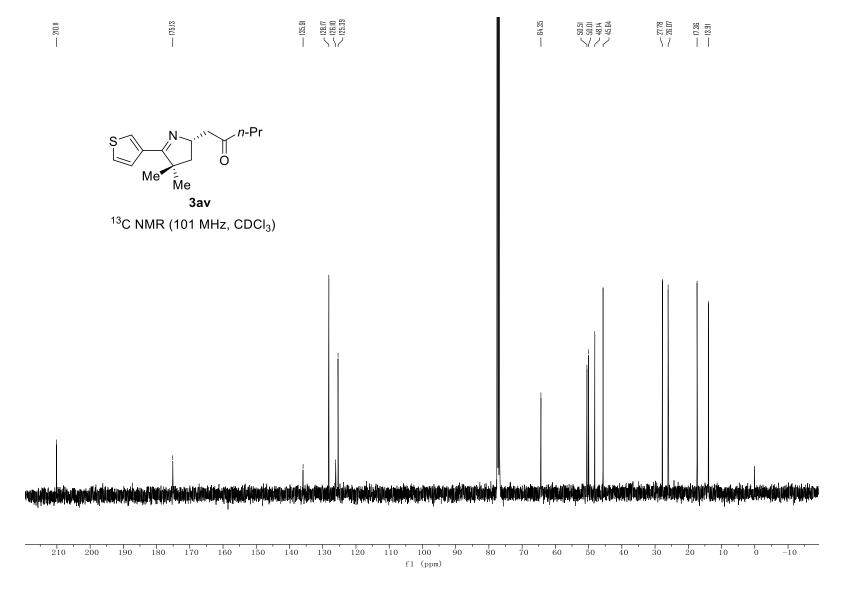


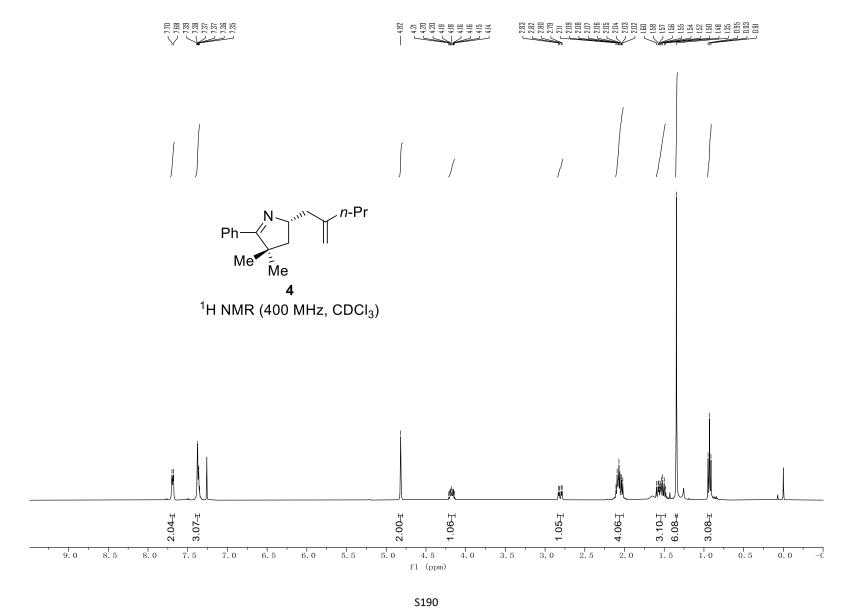


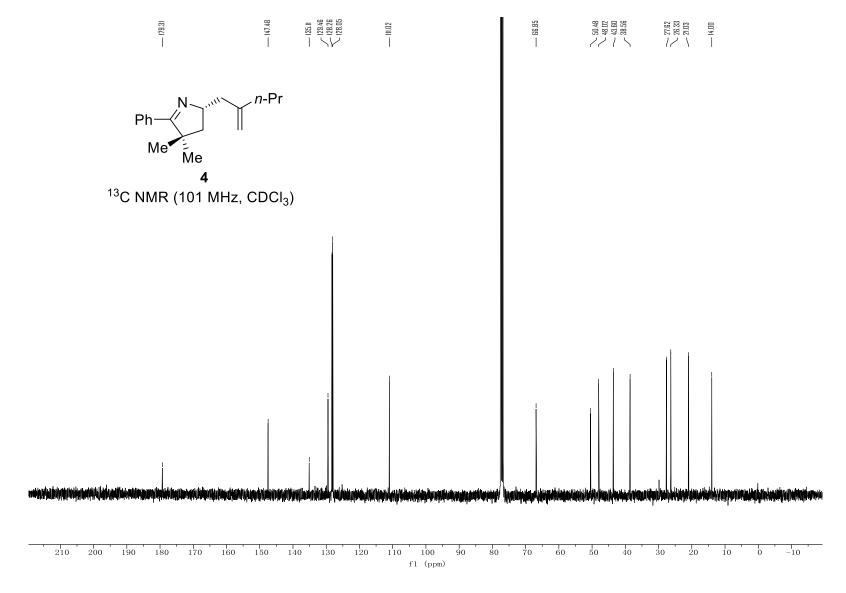


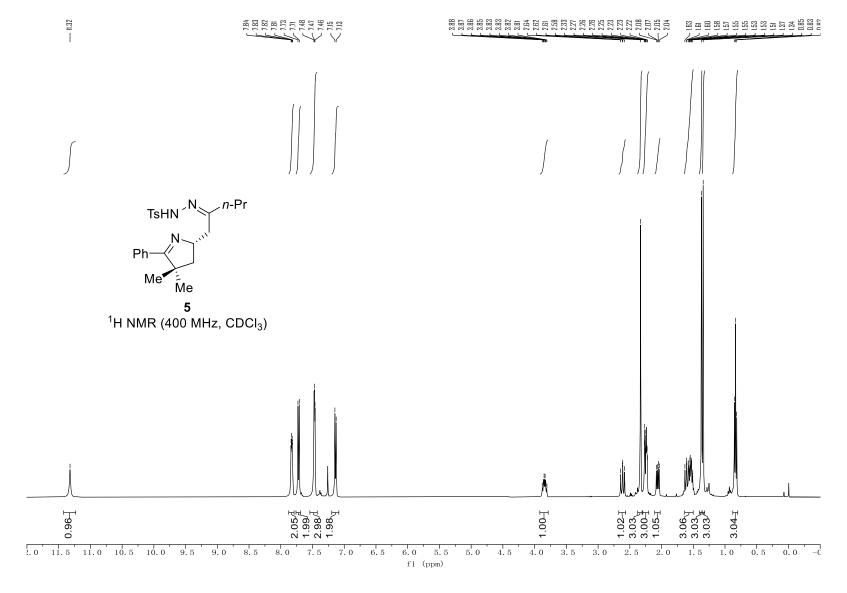


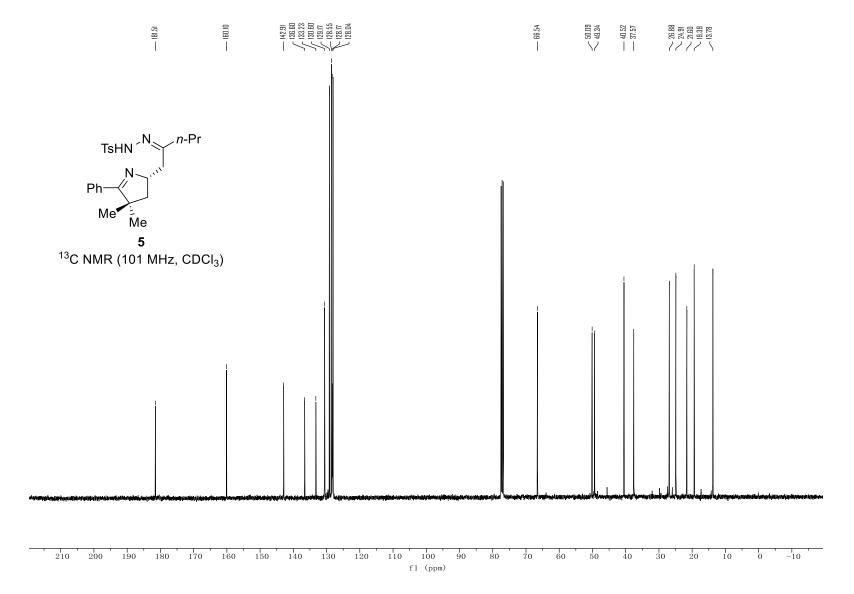


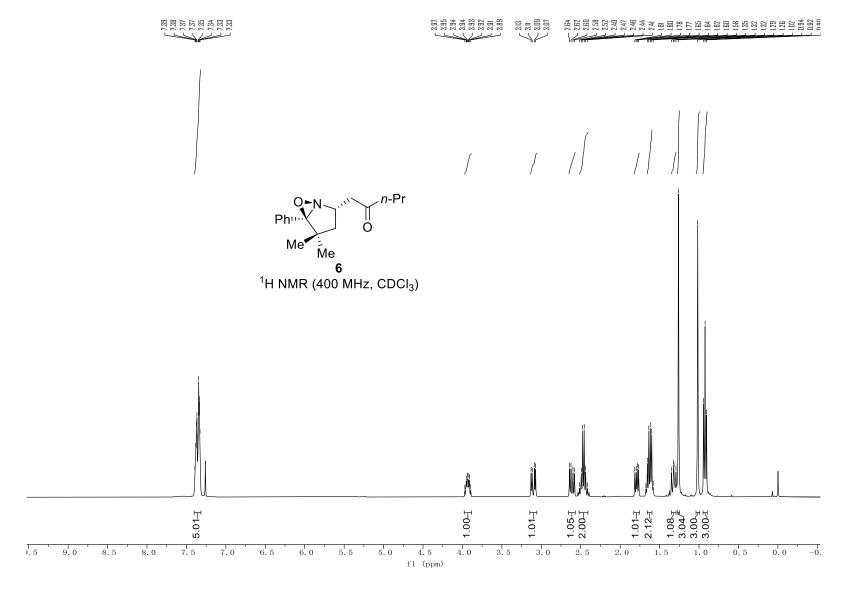


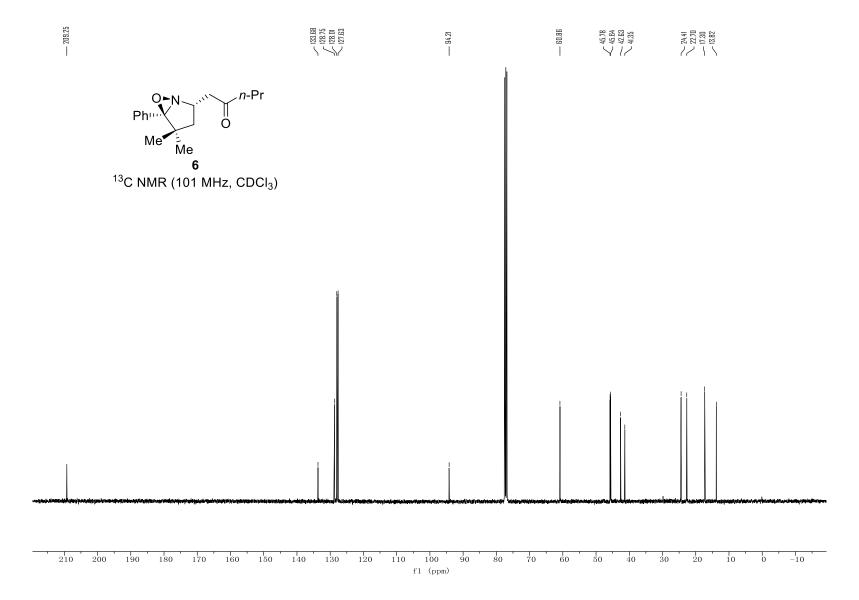


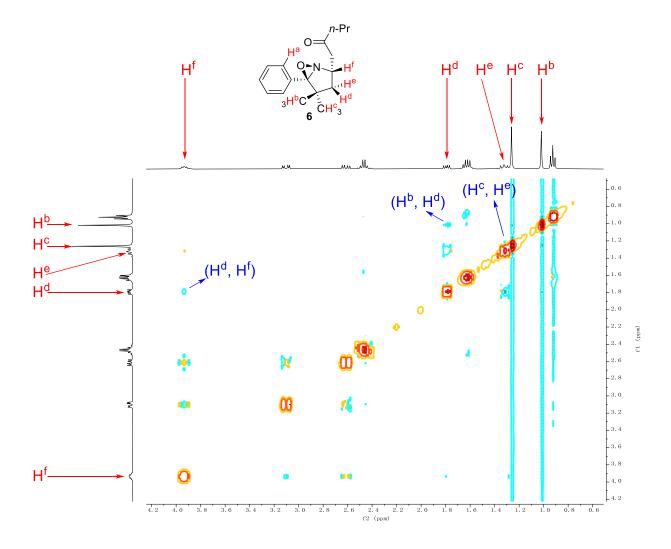


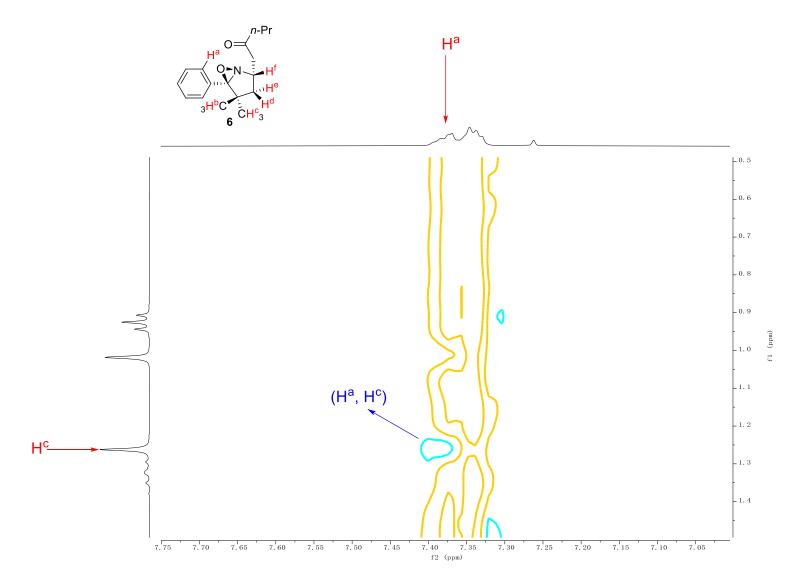


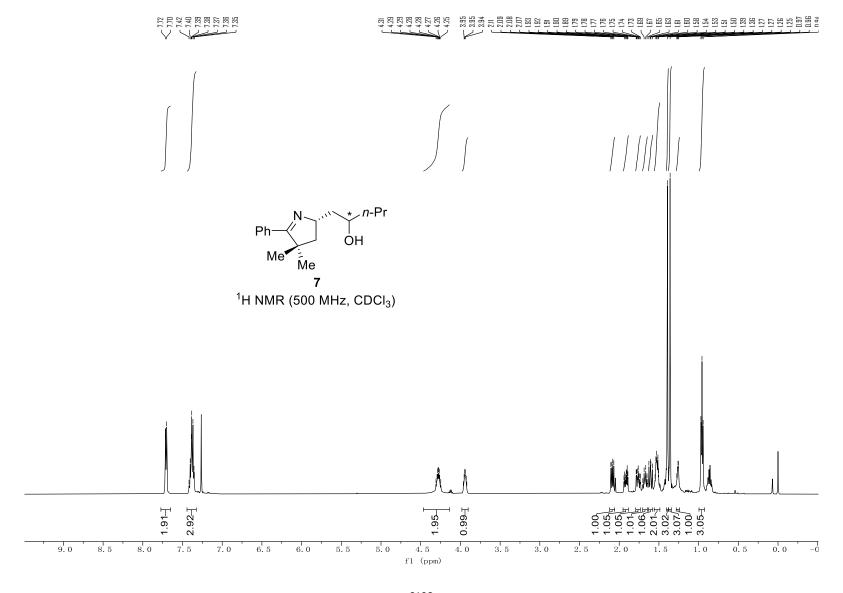


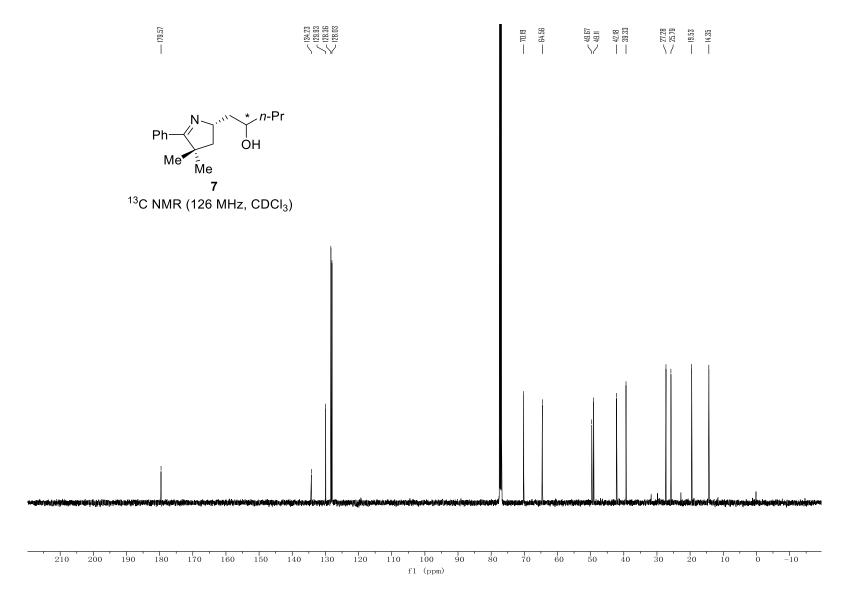


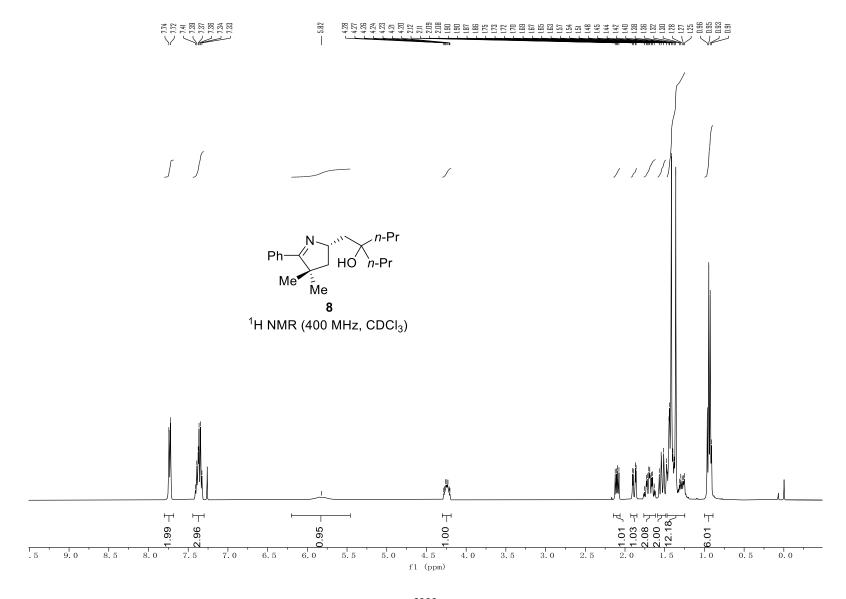


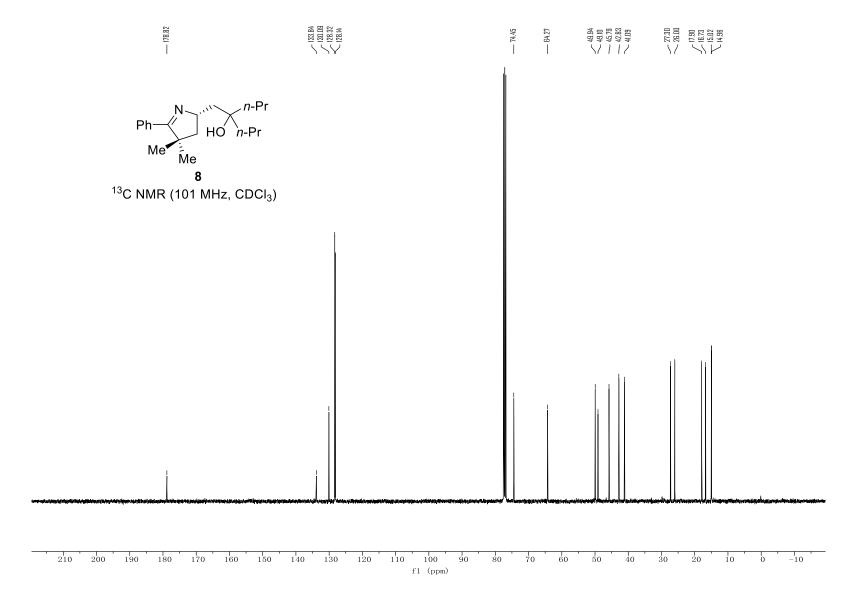


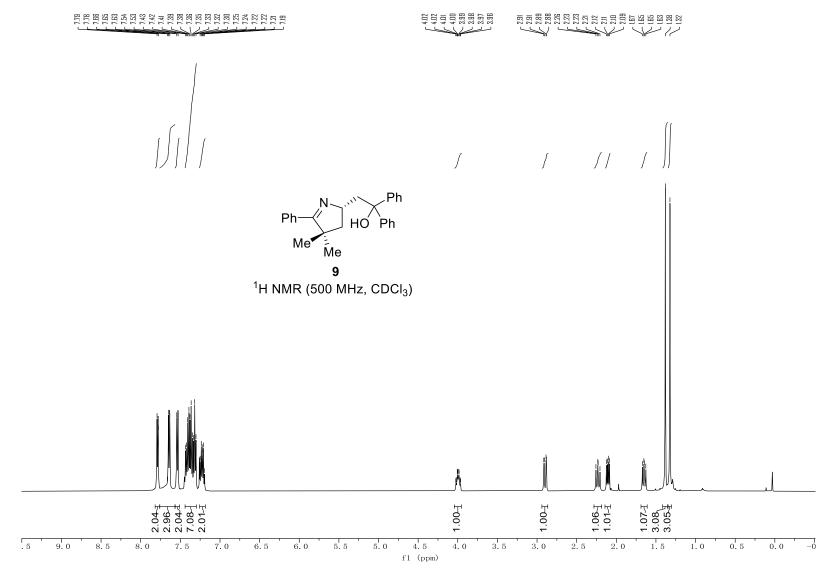


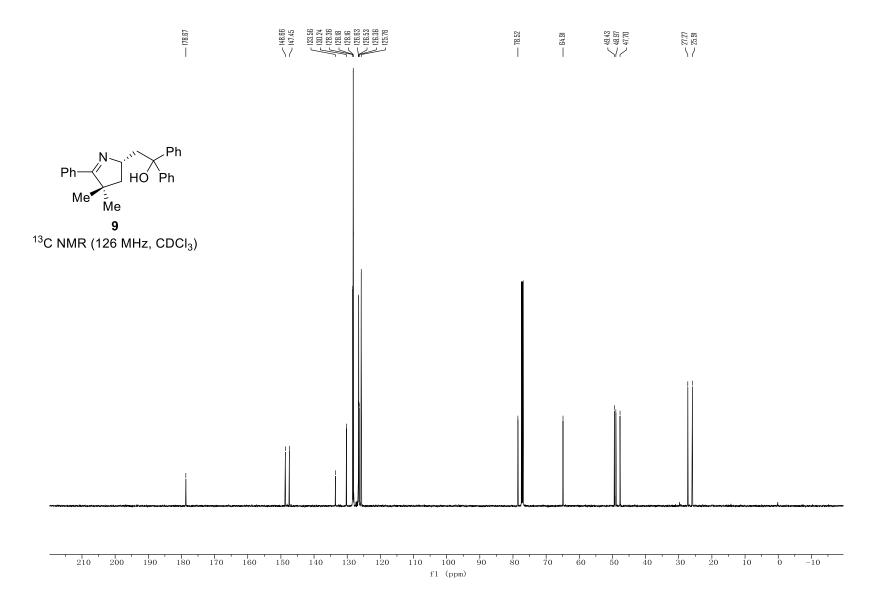


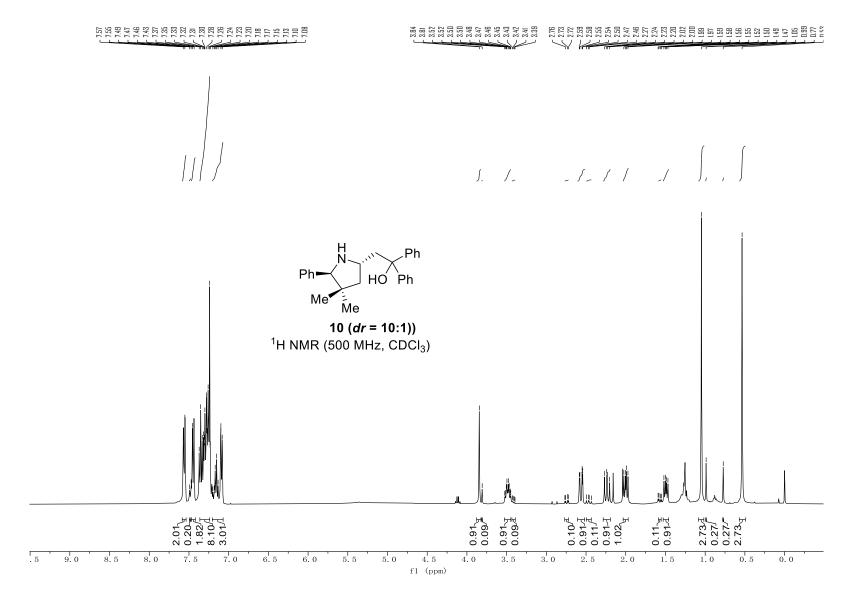


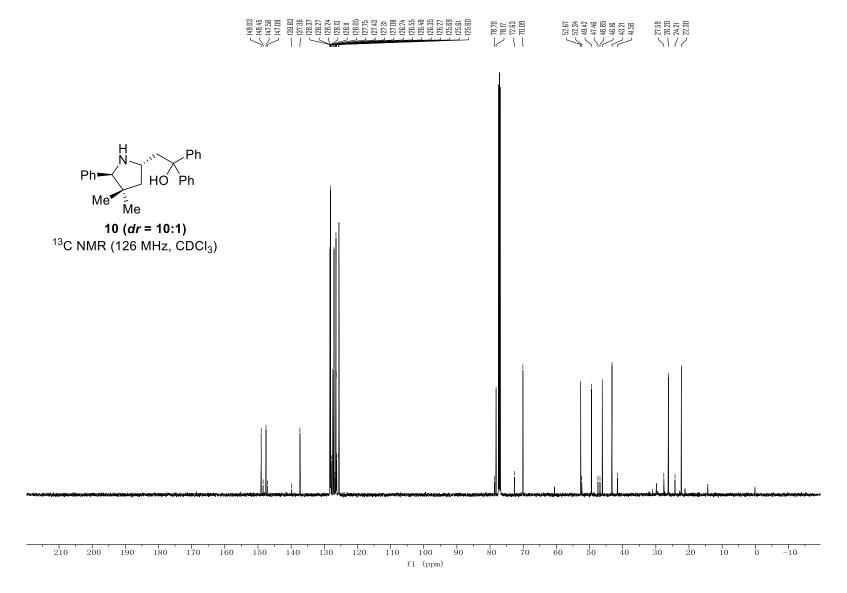


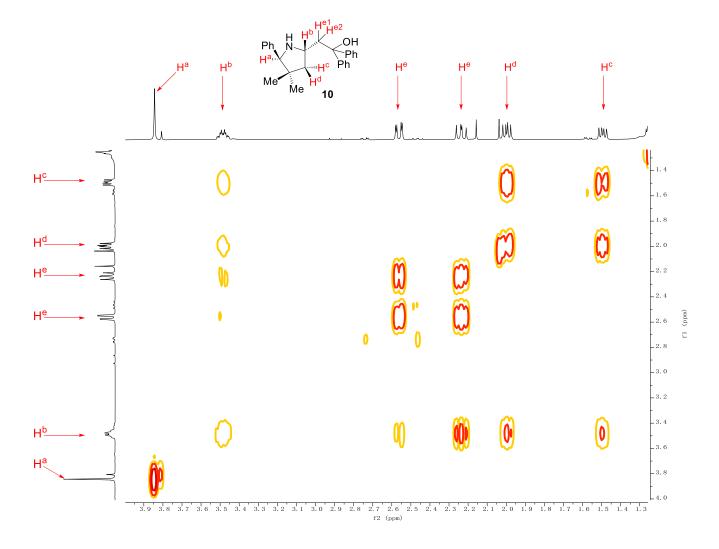


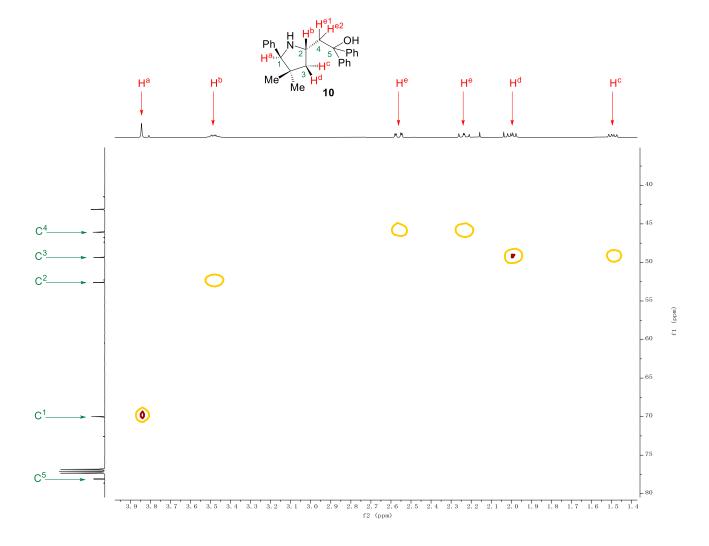


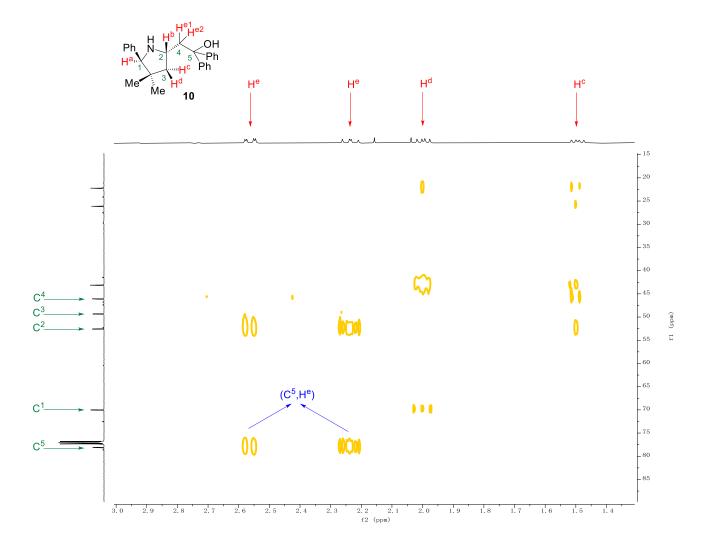


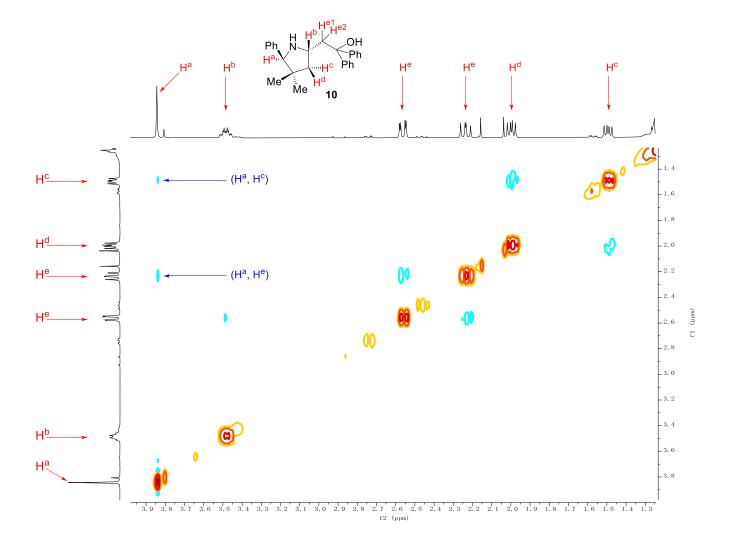


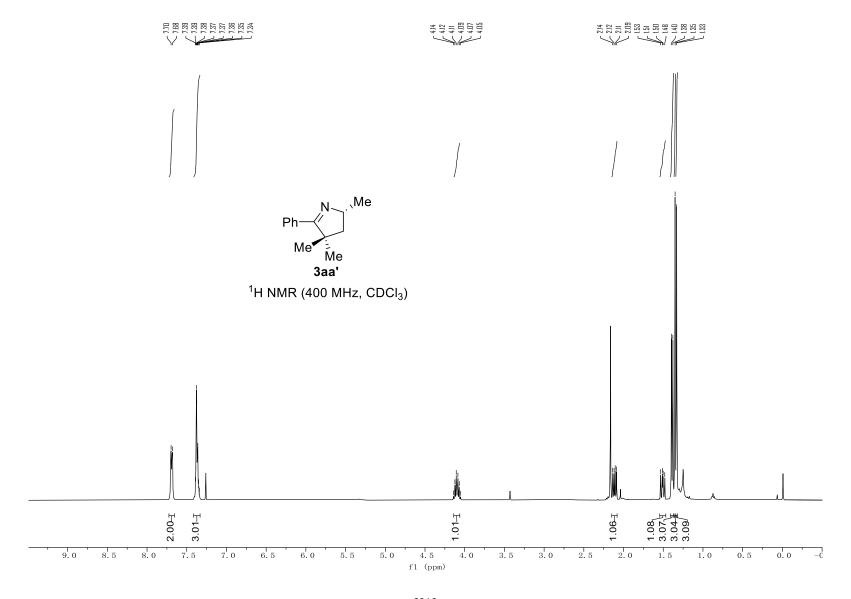


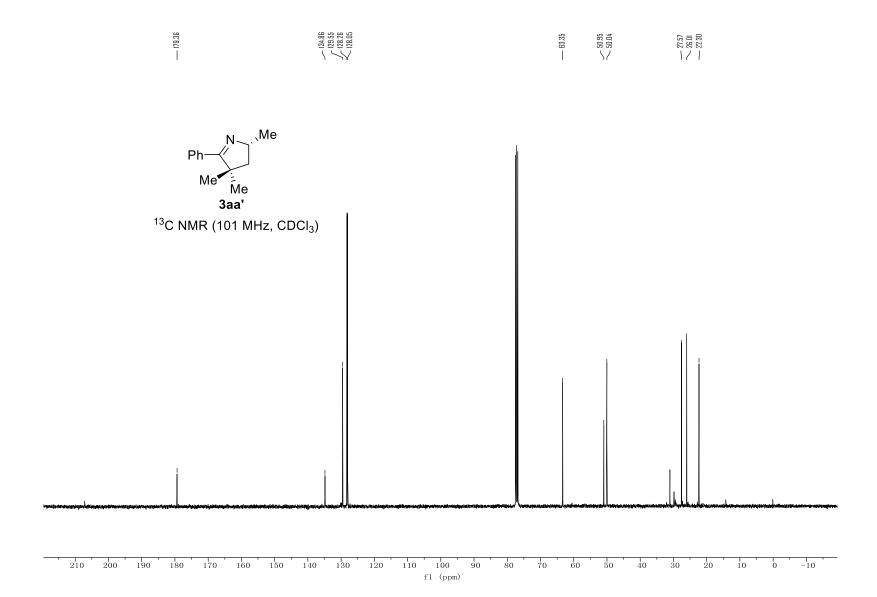


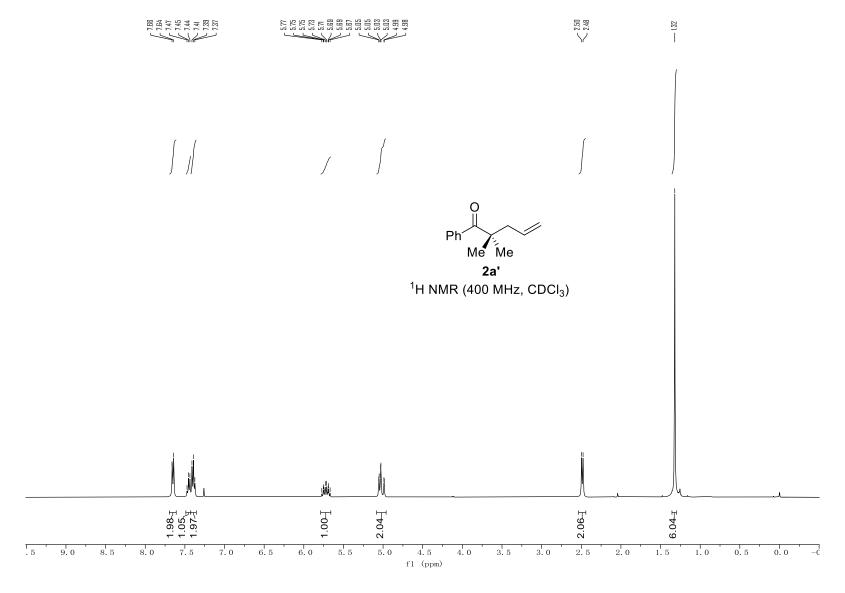


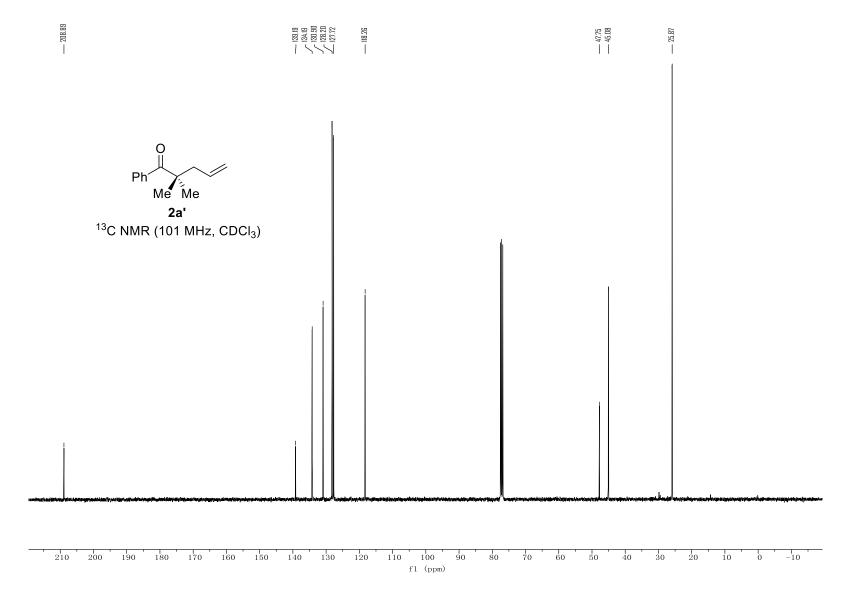




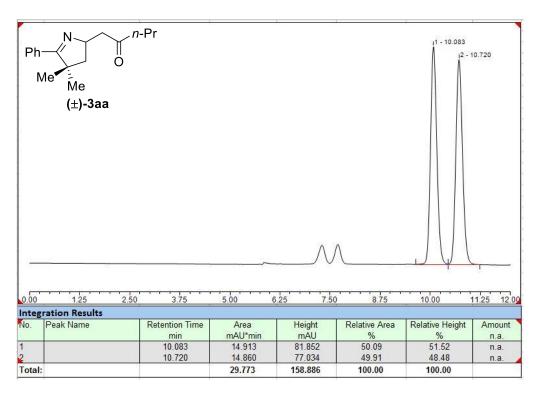


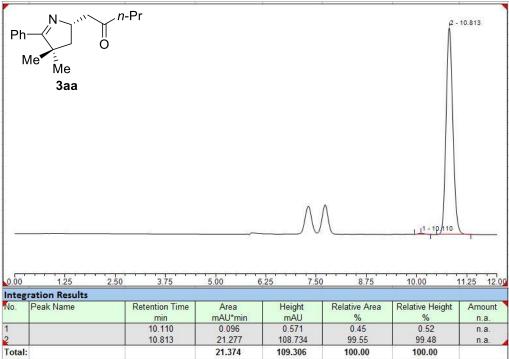






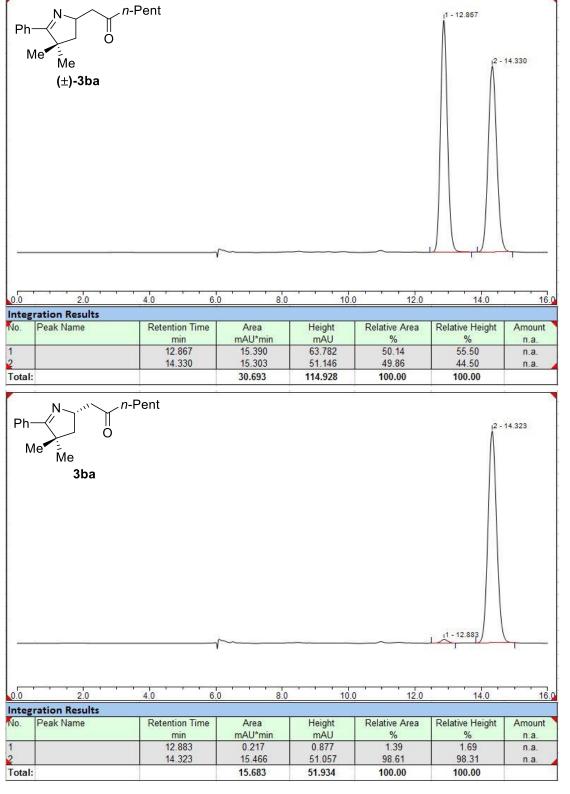
HPLC Chromatograms





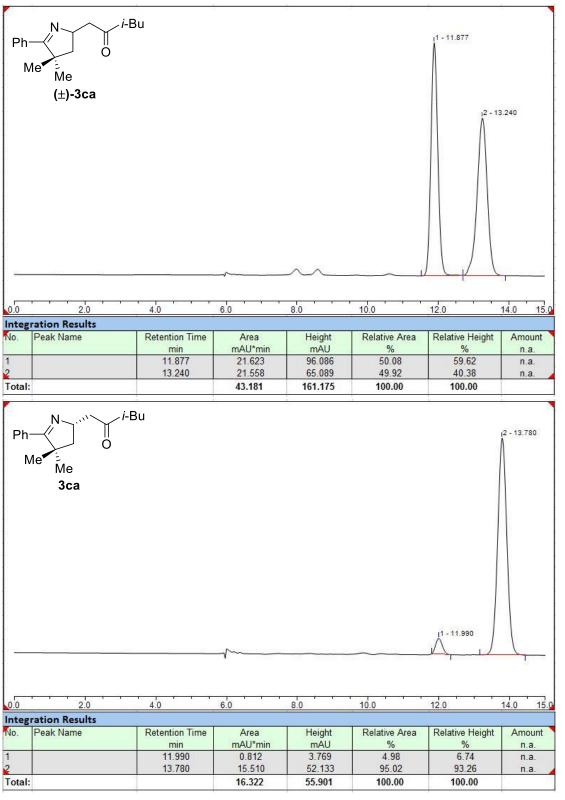
HPLC (Chiral MD): $t_R = 10.1$ (minor), 10.8 (major)

Condition: 90:10, n-Hexane:i-PrOH, flow rate 0.5 mL/min, 25 °C, 254 nm.



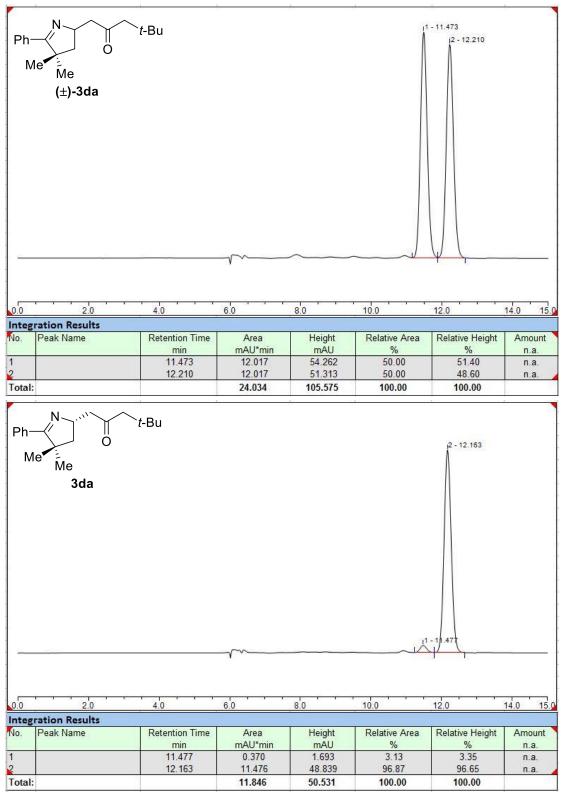
HPLC (Chiral MD): $t_R = 12.9$ (minor), 14.3 (major)

Condition: 95:5, *n*-Hexane:*i*-PrOH, flow rate 0.5 mL/min, 25 °C, 254 nm.

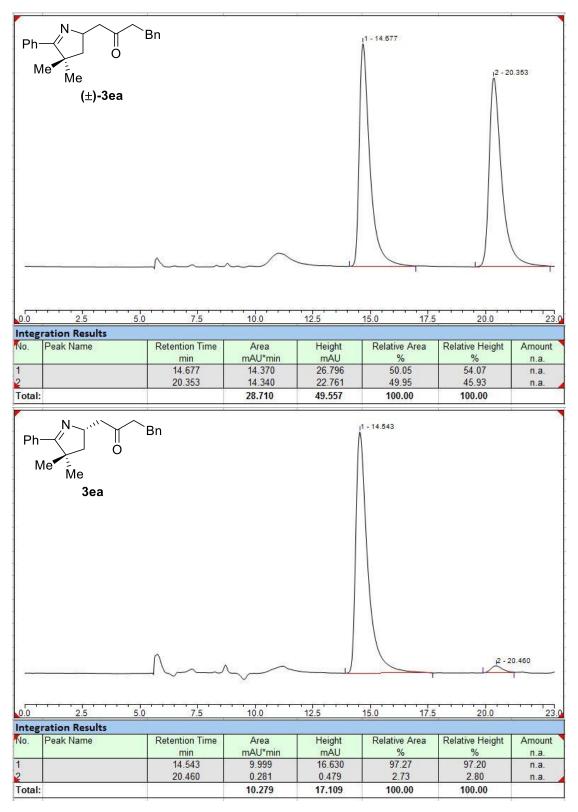


HPLC (Chiral MD): $t_R = 12.0$ (minor), 13.8 (major)

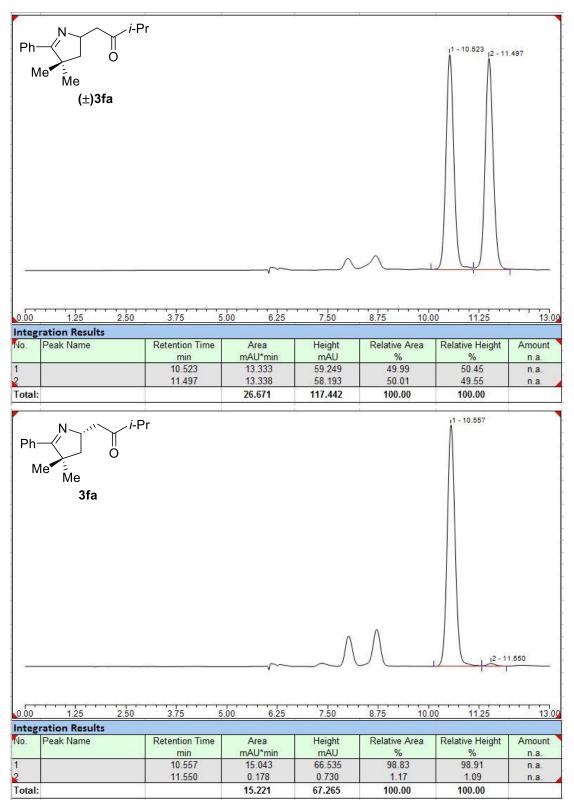
Condition: 95:5, *n*-Hexane:*i*-PrOH, flow rate 0.5 mL/min, 25 °C, 254 nm.



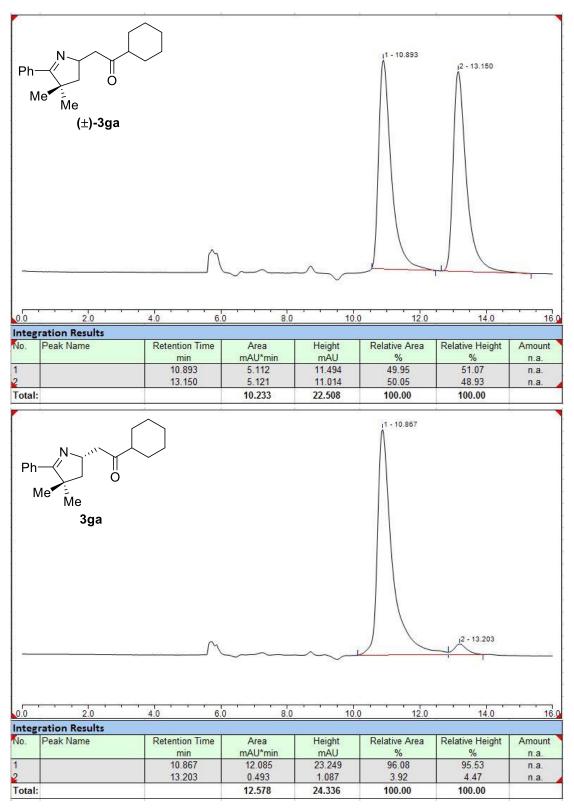
HPLC (Chiral MD): $t_R = 11.5$ (minor), 12.2 (major)



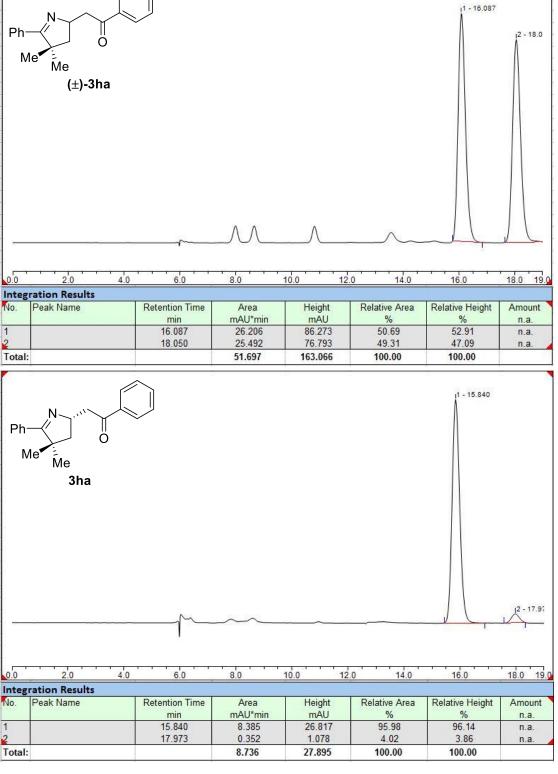
HPLC (Chiralpak IA): t_R = 14.5 (major), 20.5 (minor)



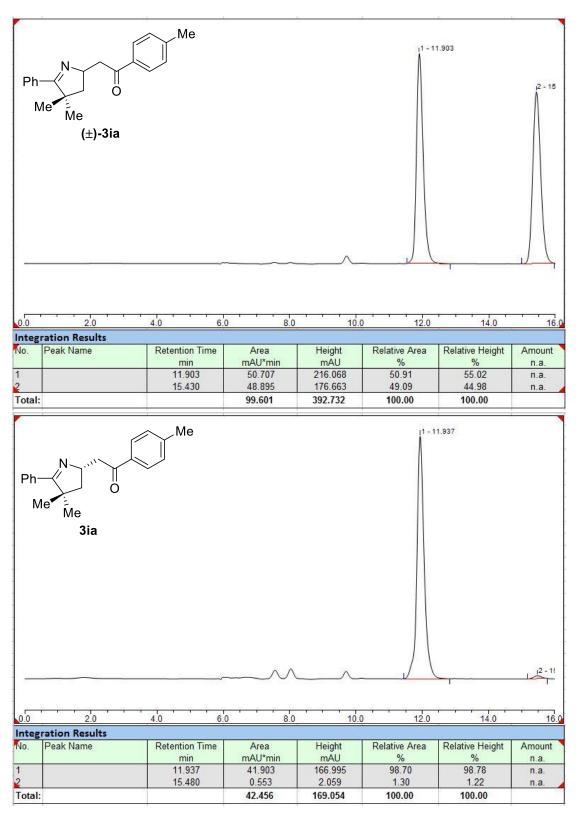
HPLC (Chiral MD): $t_R = 10.6$ (major), 11.6 (minor)



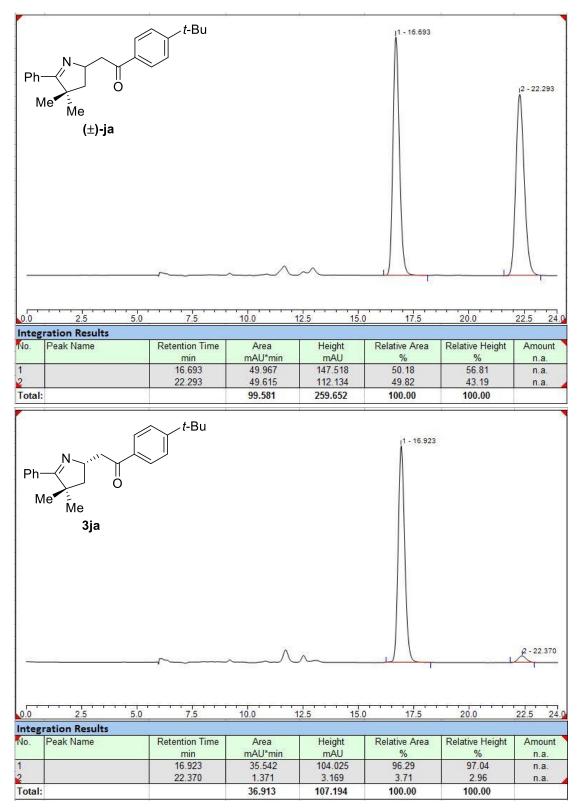
HPLC (Chiralpak IA): $t_R = 10.9$ (major), 13.2 (minor)



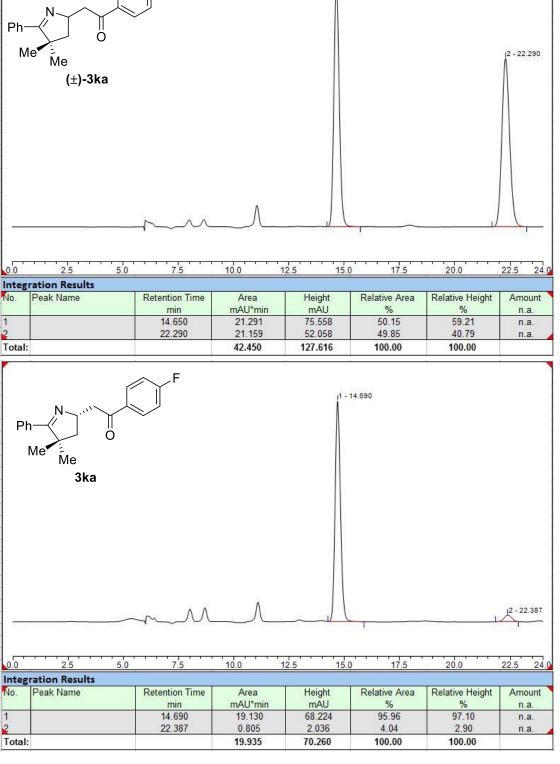
HPLC (Chiral MD): $t_R = 15.8$ (major), 18.0 (minor)



HPLC (Chiral MD): $t_R = 11.9$ (major), 15.5 (minor)

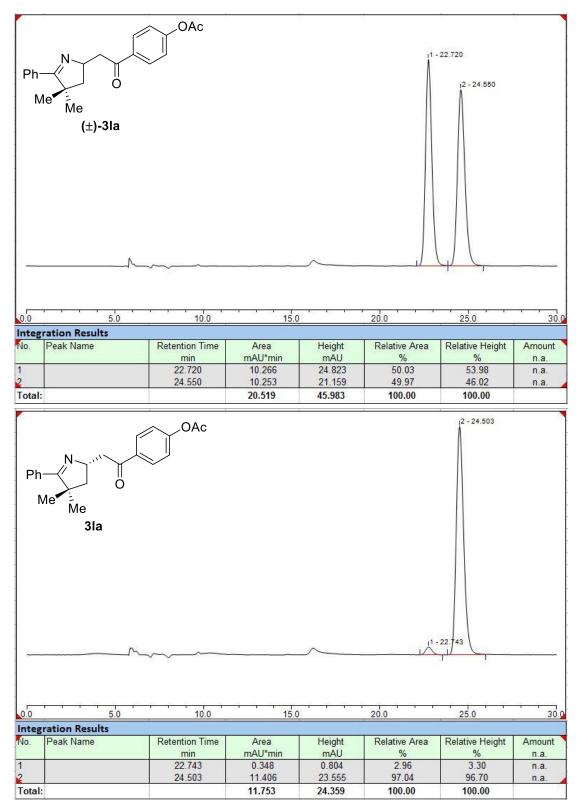


HPLC (Chiral MD): $t_R = 16.9$ (major), 22.4 (minor)

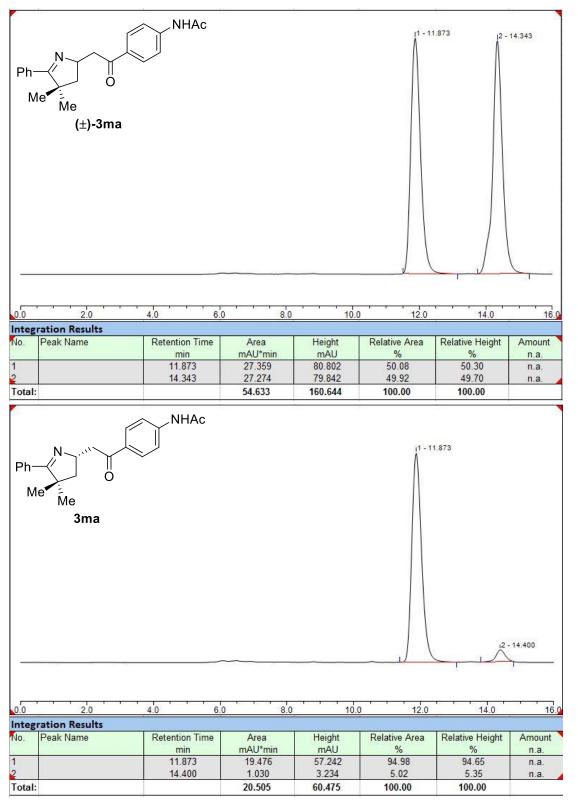


1 - 14.650

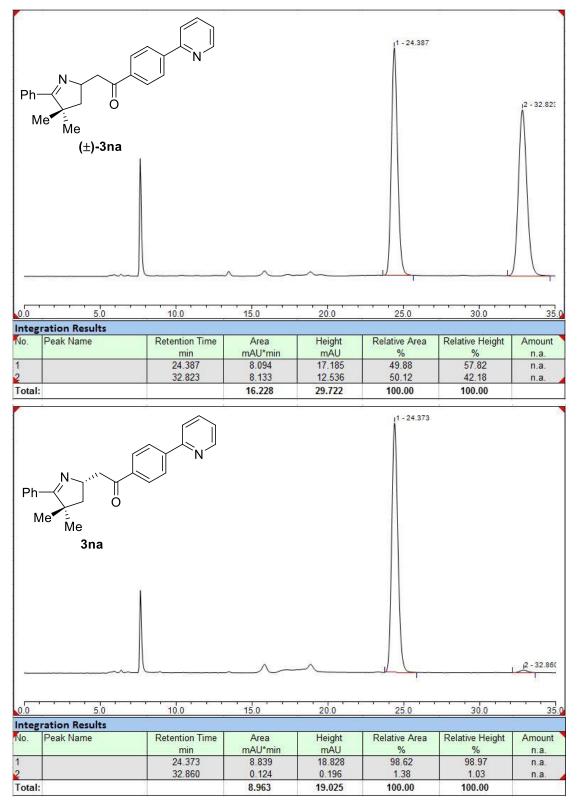
HPLC (Chiral MD): $t_R = 14.7$ (major), 22.4 (minor)



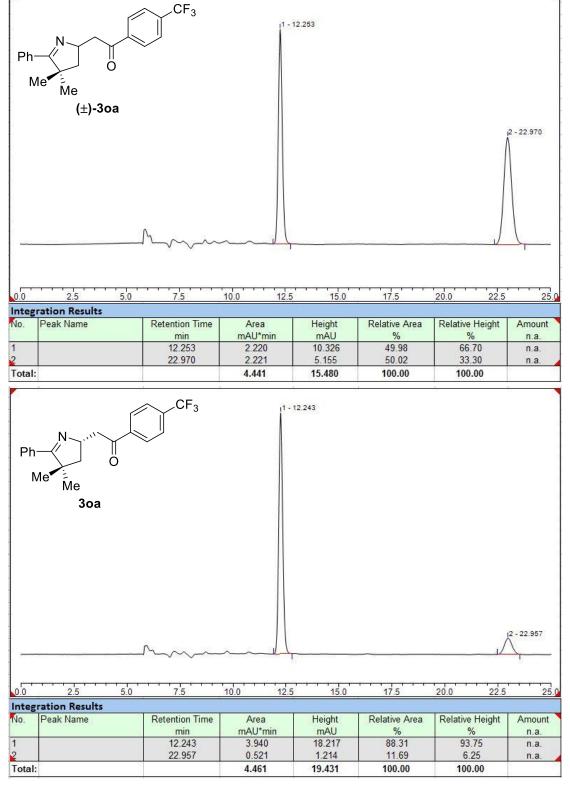
HPLC (Chiral MD): $t_R = 22.7$ (minor), 24.5 (major)



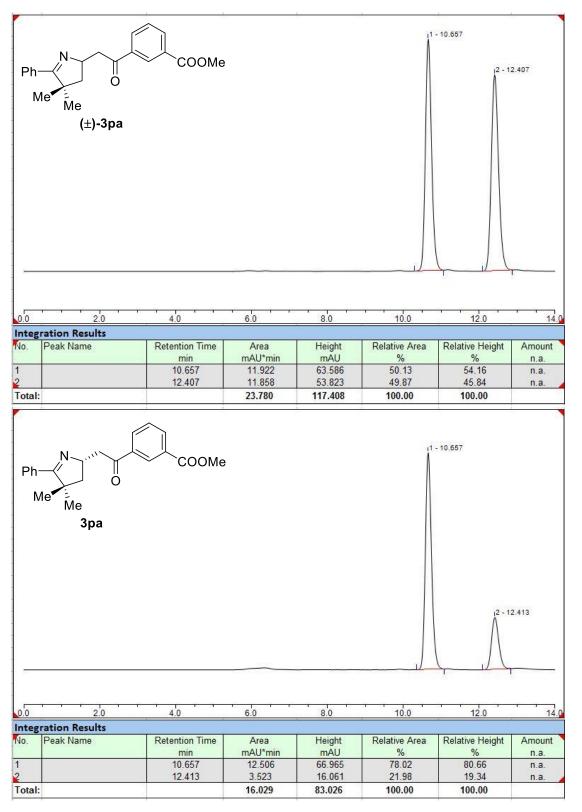
HPLC (Chiral MD): $t_R = 11.9$ (major), 14.4 (minor)



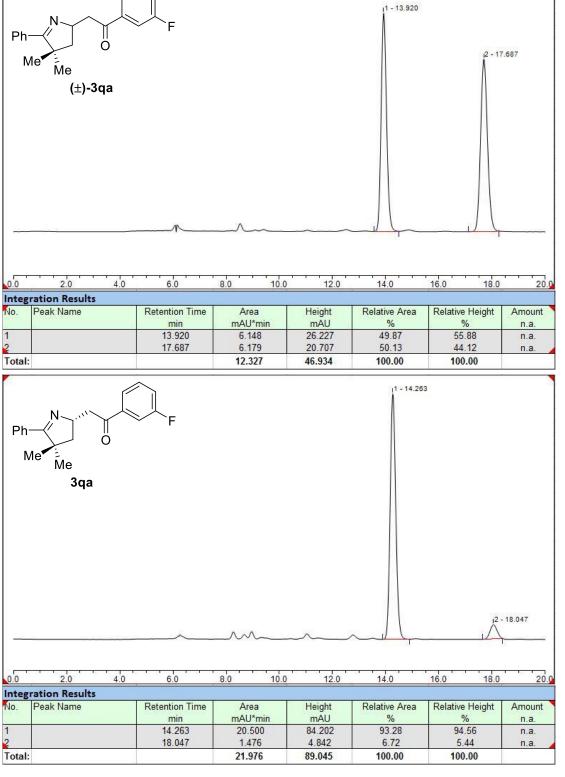
HPLC (Chiral MD): $t_R = 24.4$ (major), 32.9 (minor)



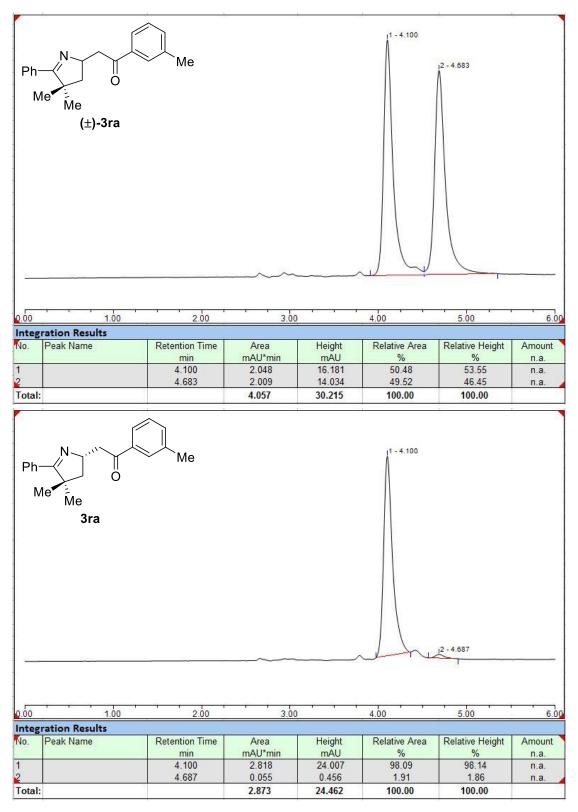
HPLC (Chiral MD): $t_R = 12.2$ (major), 23.0 (minor)



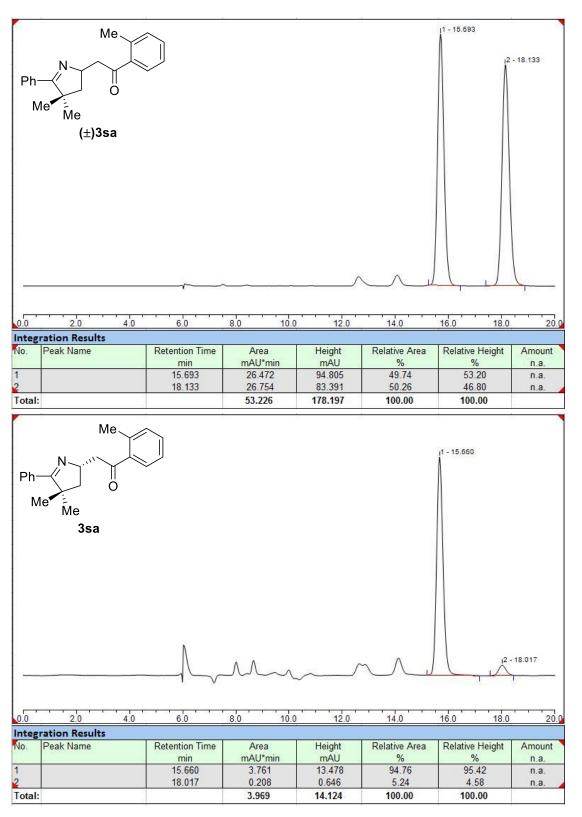
HPLC (Chiral MD): $t_R = 10.7$ (major), 12.4 (minor)



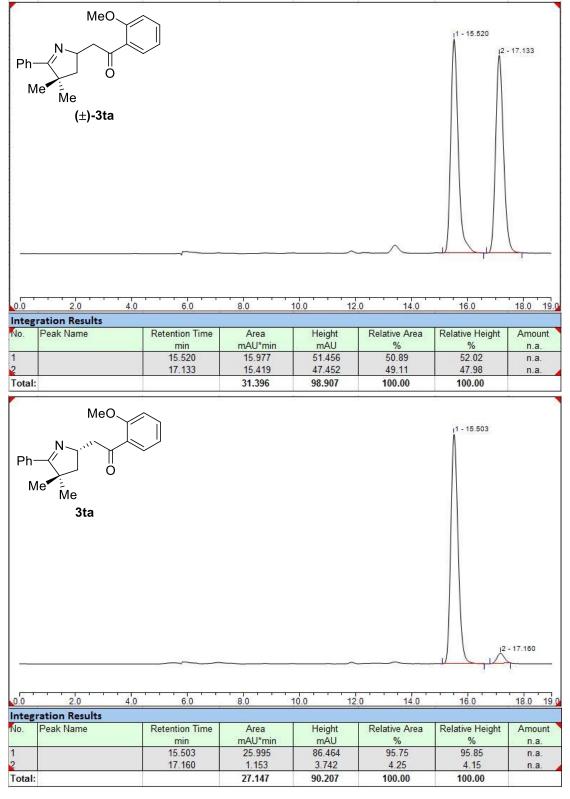
HPLC (Chiral MD): $t_R = 14.3$ (major), 18.0 (minor)



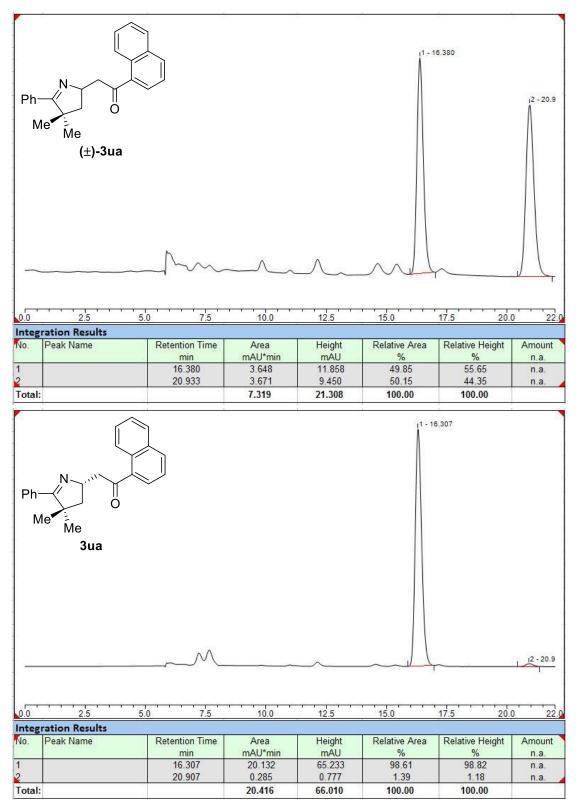
HPLC (Chiralpak IA): t_R = 4.1 (major), 4.7 (minor)



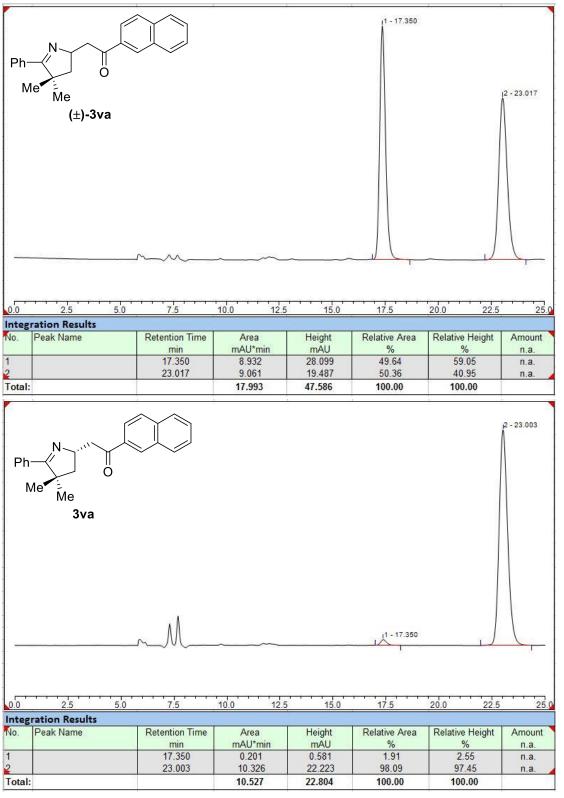
HPLC (Chiral MD): $t_R = 15.7$ (major), 18.0 (minor)



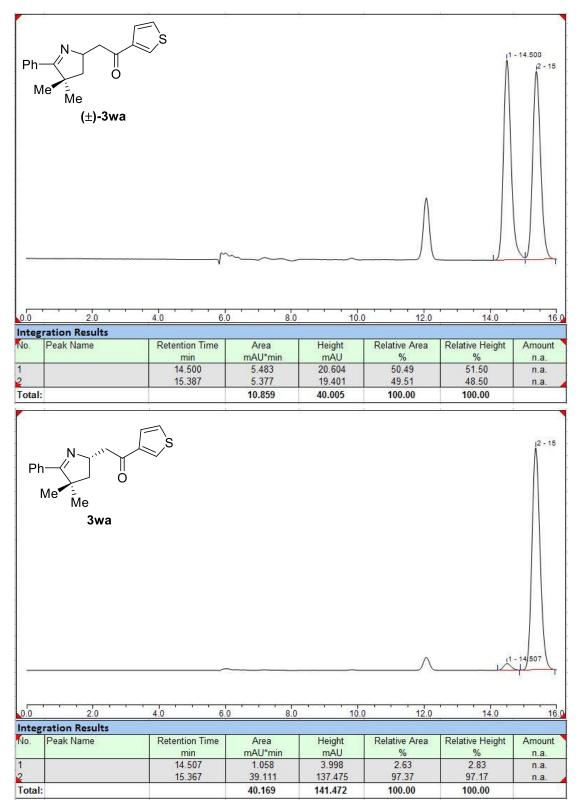
HPLC (Chiral MD): $t_R = 15.5$ (major), 17.2 (minor)



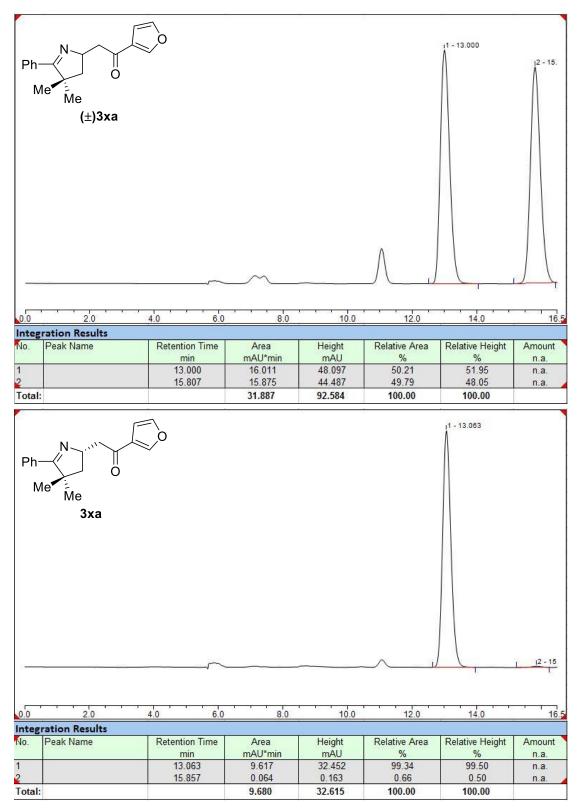
HPLC (Chiral MD): $t_R = 16.3$ (major), 20.9 (minor)



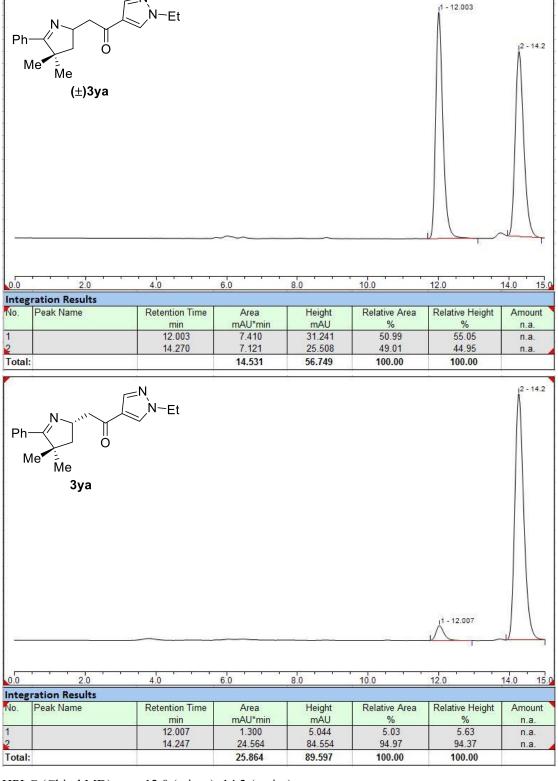
HPLC (Chiral MD): $t_R = 17.4$ (major), 23.0 (minor)



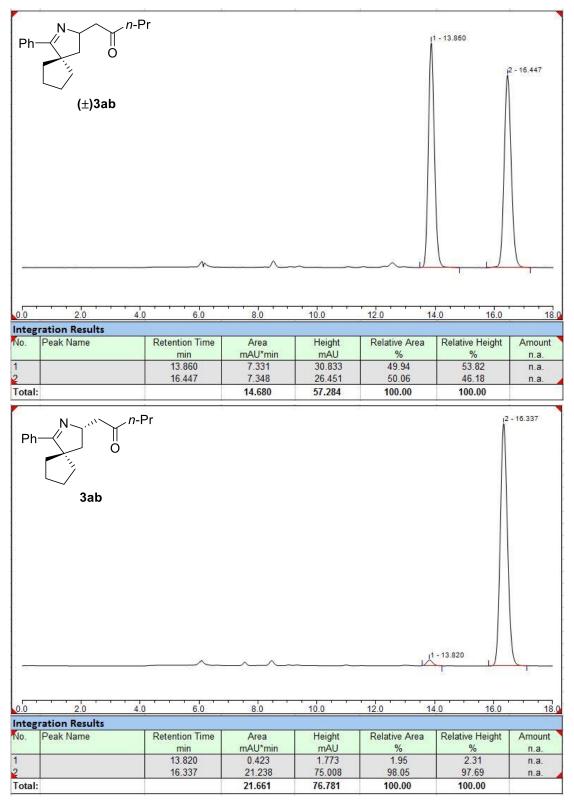
HPLC (Chiral MD): $t_R = 14.5$ (minor), 15.4 (major)



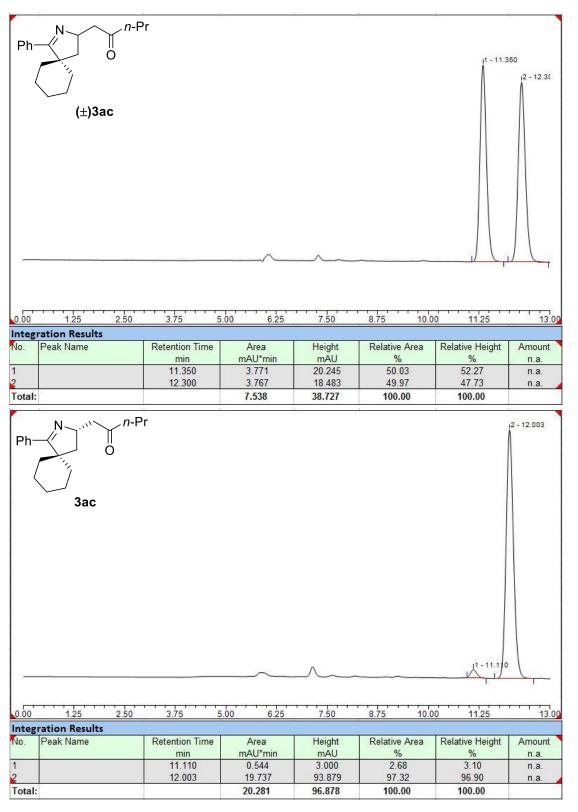
HPLC (Chiralpak AD-H): $t_R = 13.1$ (major), 15.9 (minor)



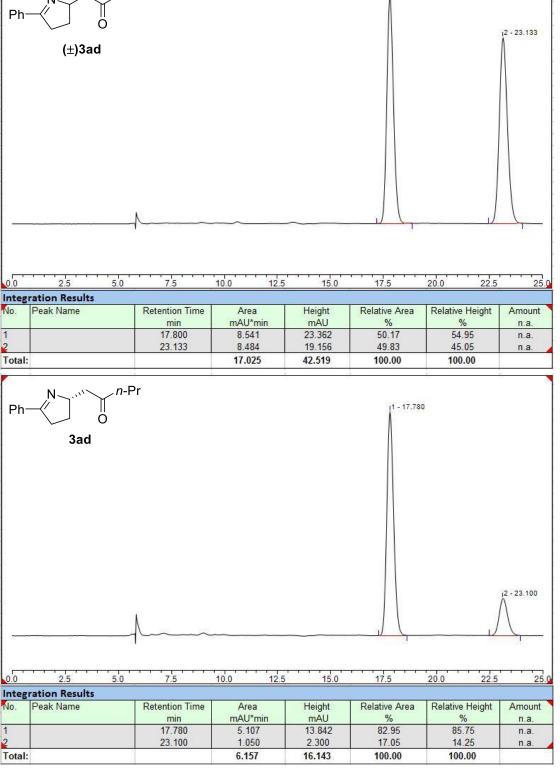
HPLC (Chiral MD): $t_R = 12.0$ (minor), 14.2 (major)



HPLC (Chiral MD): $t_R = 13.8$ (minor), 16.3 (major)

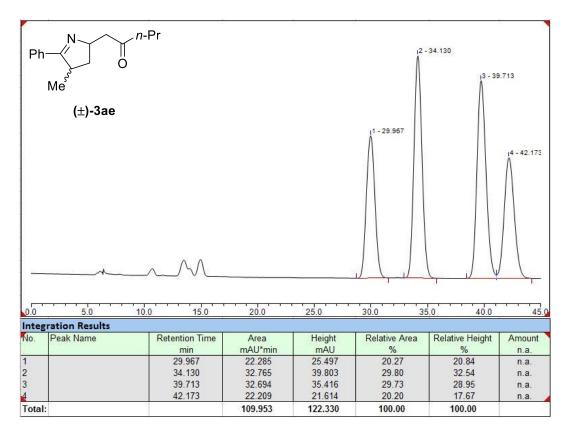


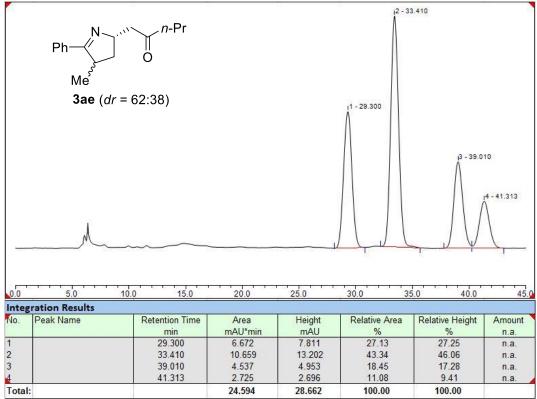
HPLC (Chiral MD): $t_R = 11.1$ (minor), 12.0 (major)



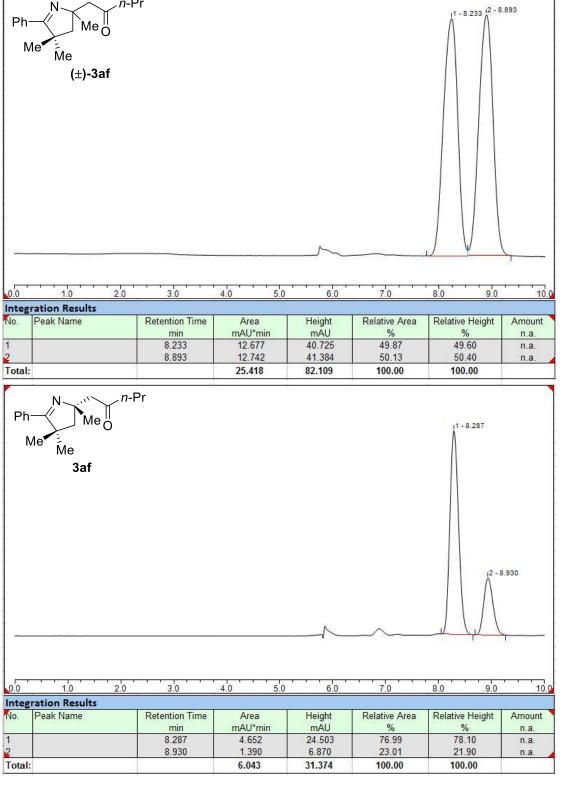
1 - 17.800

HPLC (Chiralpak AD-H): $t_R = 17.8$ (major), 23.1 (minor)

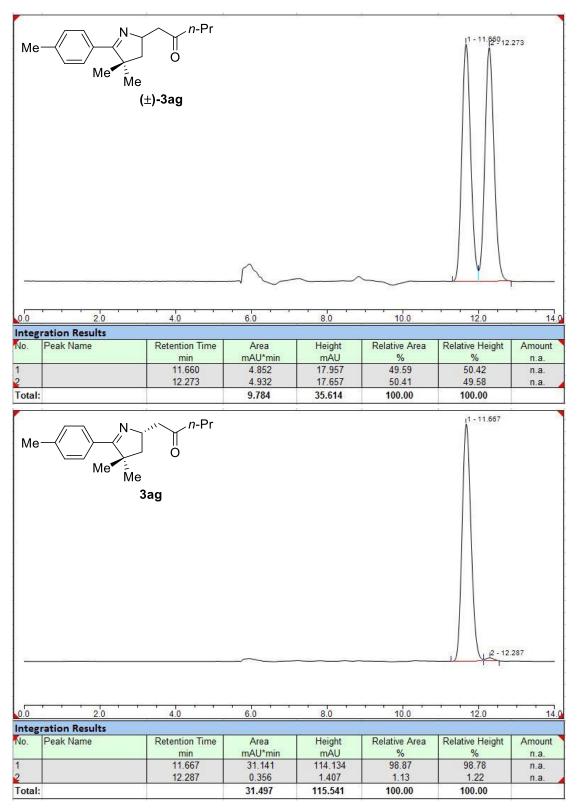




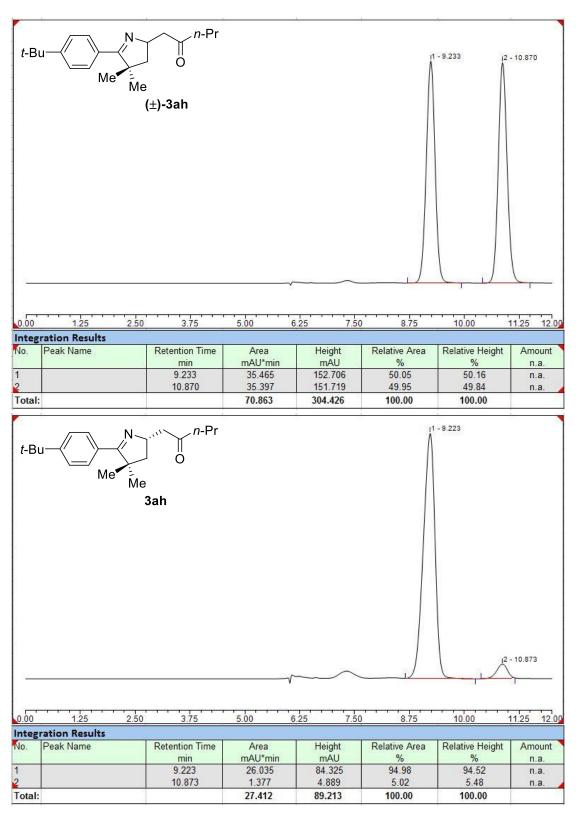
HPLC (Chiralpak AD-H): t_R = 29.3 (major, minor diastereomer), 33.4 (major, major diastereomer), 39.0 (minor, major diastereomer), 41.3 (minor, minor diastereomer)



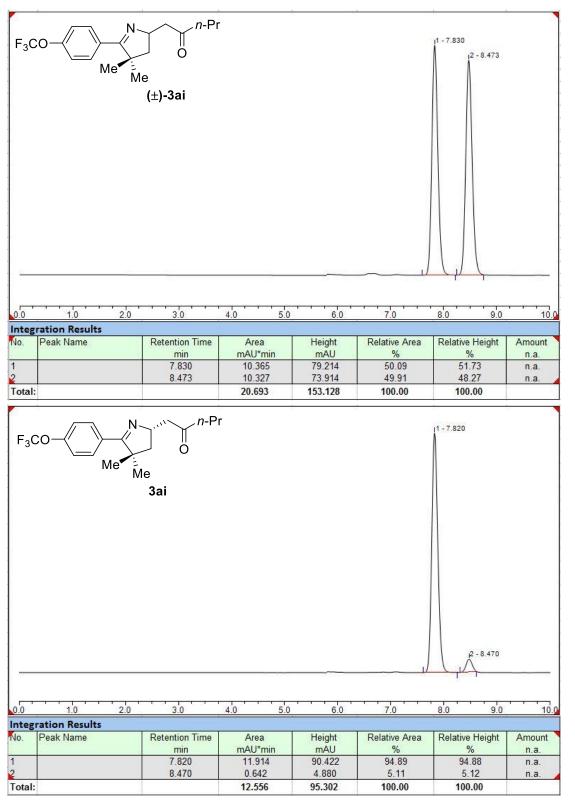
HPLC (Chiralpak AD-H): $t_R = 8.3$ (major), 8.9 (minor)



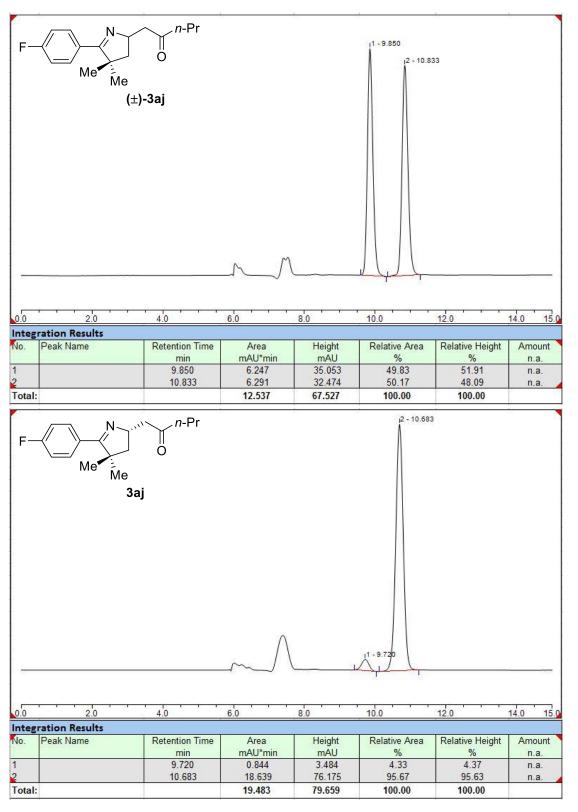
HPLC (Chiralpak AD-H): $t_R = 11.7$ (major), 12.3 (minor)



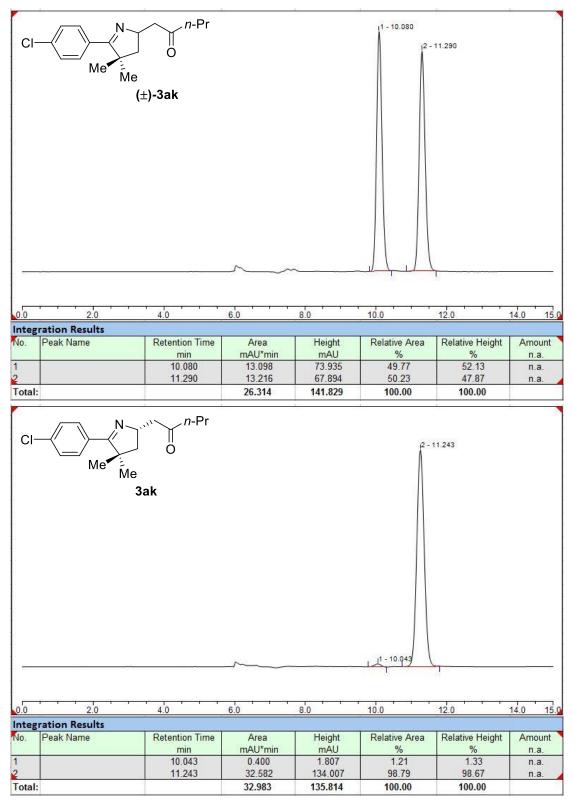
HPLC (Chiral MD): $t_R = 9.2$ (major), 10.9 (minor)



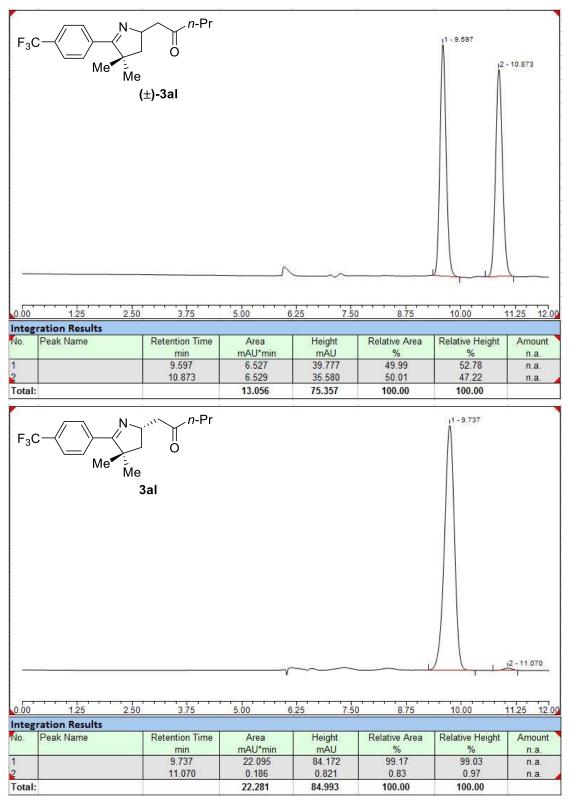
HPLC (Chiral MD): $t_R = 7.8$ (major), 8.5 (minor)



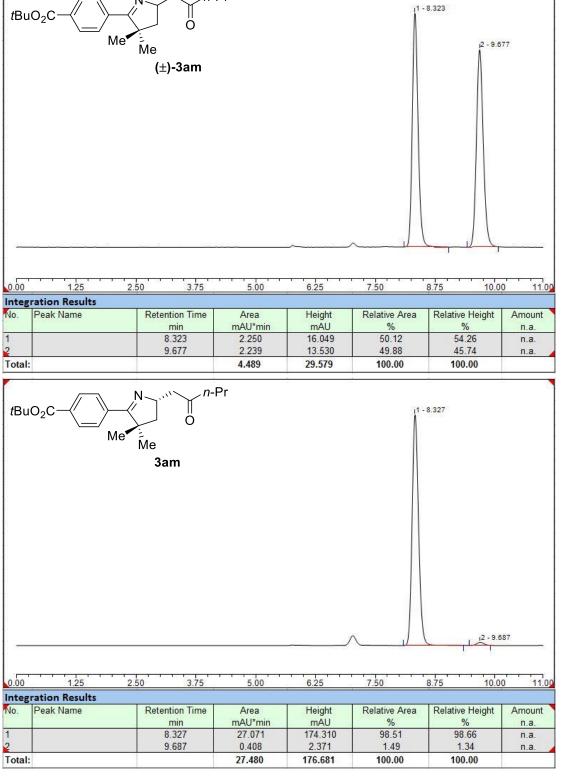
HPLC (Chiral MD): $t_R = 9.7$ (minor), 10.7 (major)



HPLC (Chiral MD): $t_R = 10.0$ (minor), 11.2 (major)

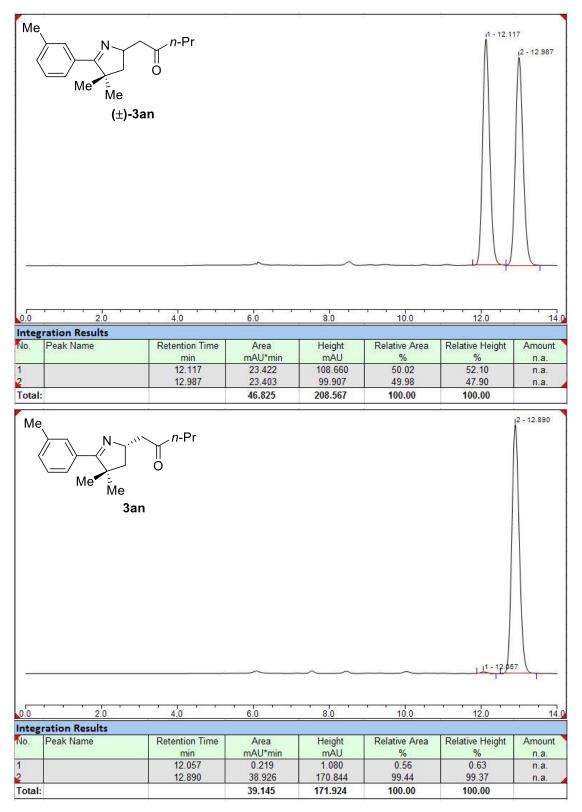


HPLC (Chiral MD): $t_R = 9.7$ (major), 11.1 (minor)

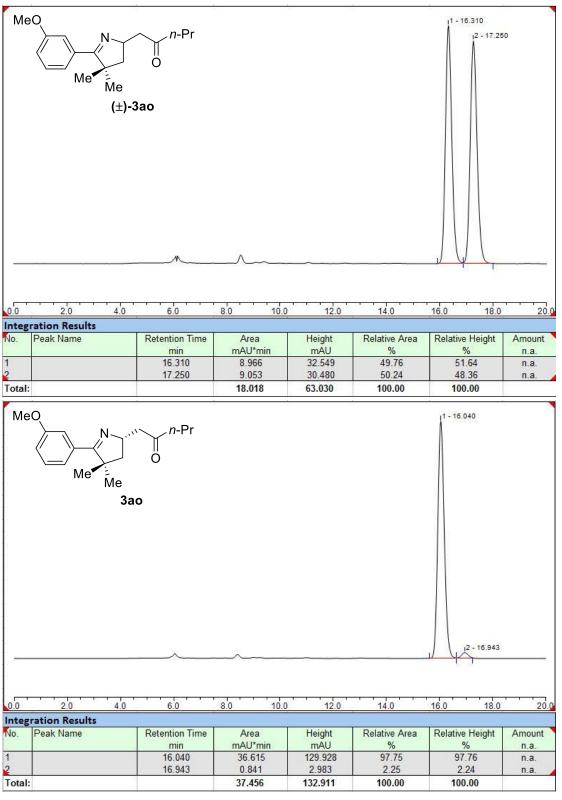


n-Pr

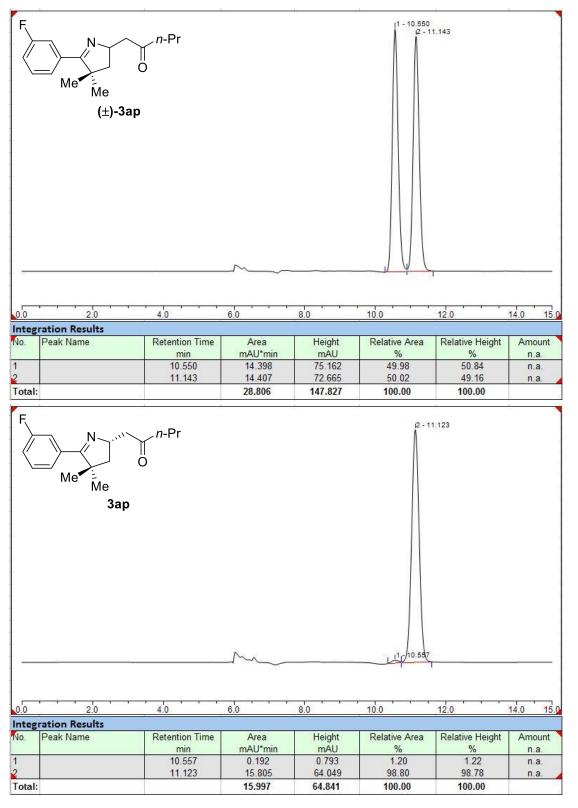
HPLC (Chiral MD): $t_R = 8.3$ (major), 9.7 (minor)



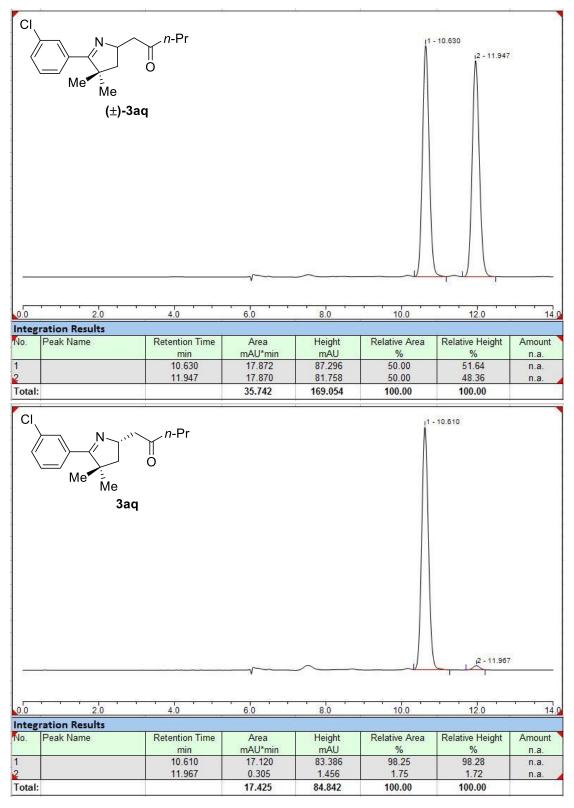
HPLC (Chiral MD): $t_R = 12.1$ (minor), 12.9 (major)



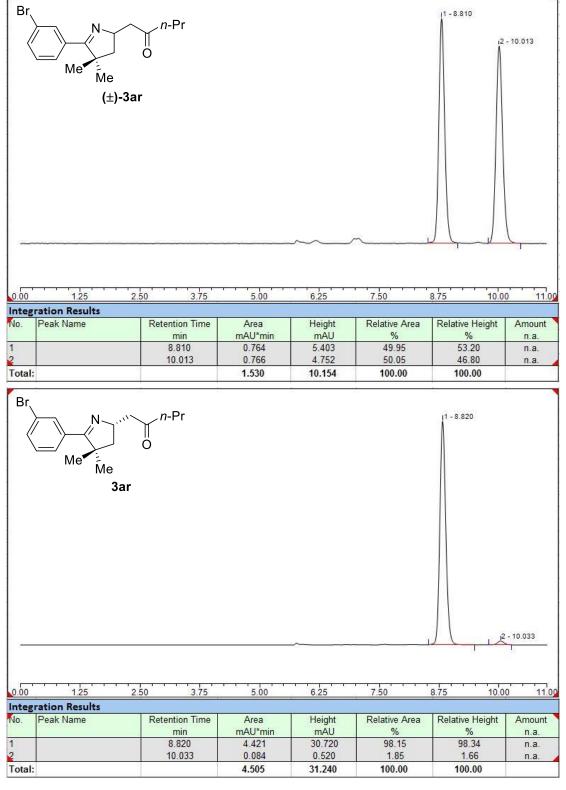
HPLC (Chiral MD): $t_R = 16.0$ (major), 16.9 (minor)



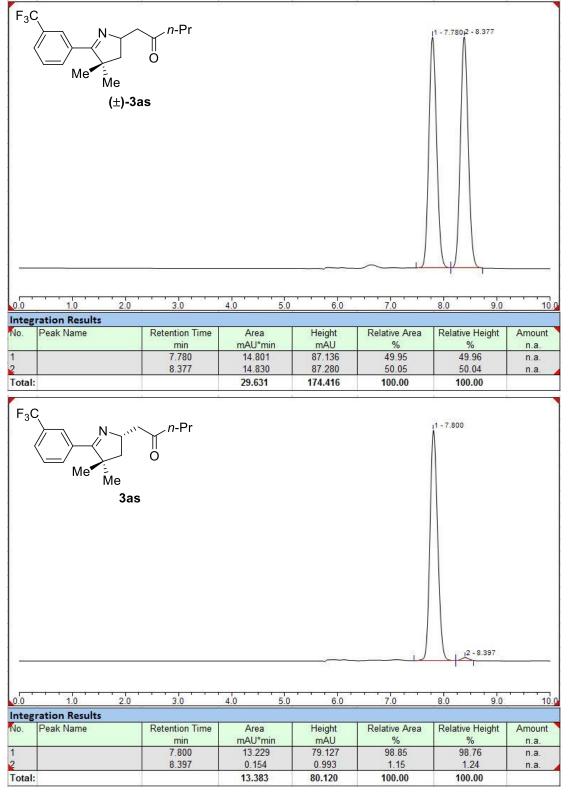
HPLC (Chiral MD): $t_R = 10.6$ (minor), 11.1 (major)



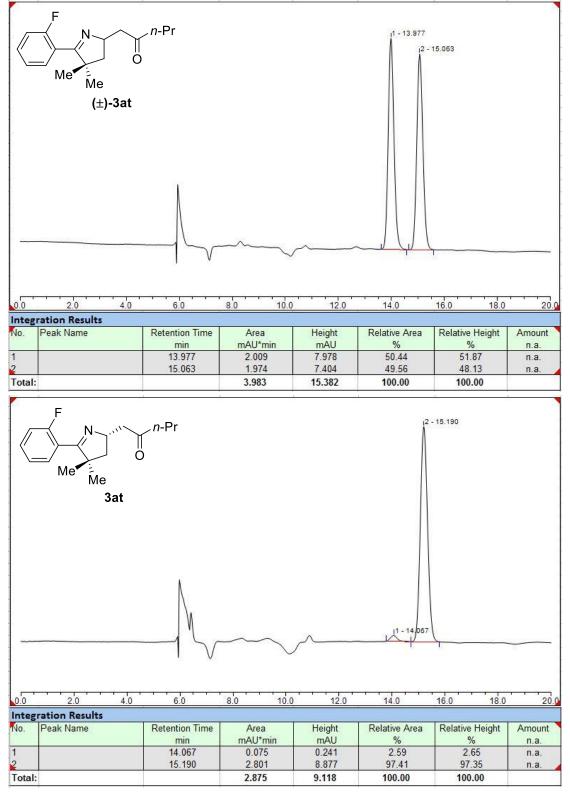
HPLC (Chiral MD): $t_R = 10.6$ (major), 12.0 (minor)



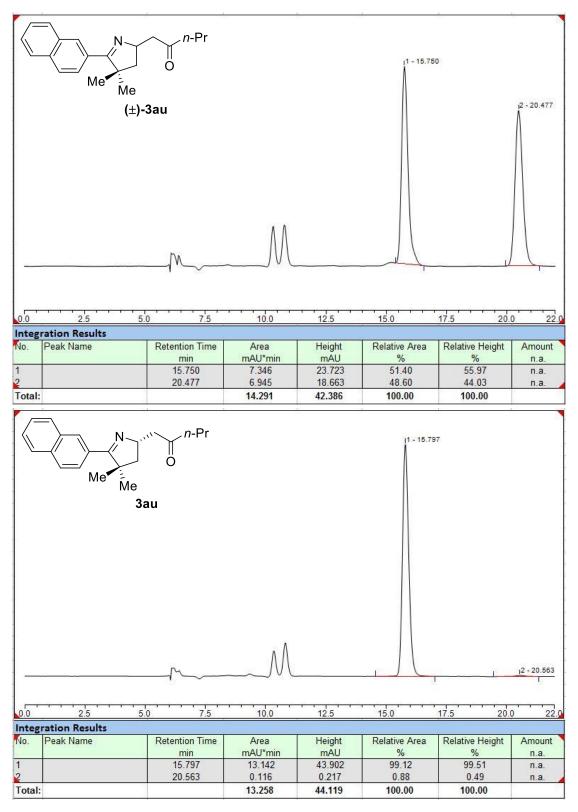
HPLC (Chiral MD): $t_R = 8.8$ (major), 10.0 (minor)



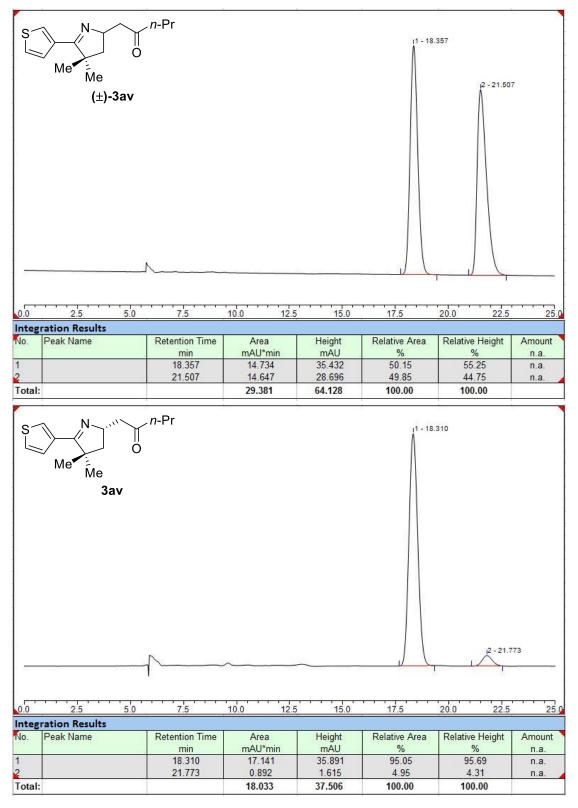
HPLC (Chiral MD): $t_R = 7.8$ (major), 8.4 (minor)



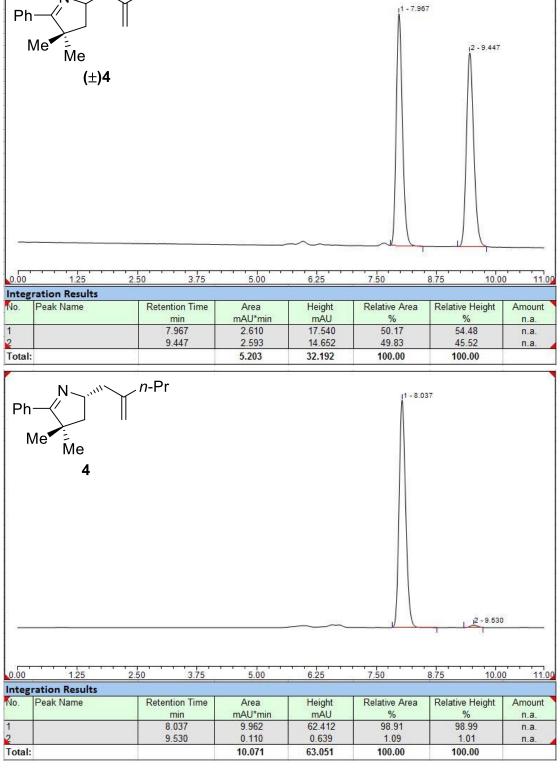
HPLC (Chiral MD): $t_R = 14.1$ (minor), 15.2 (major)



HPLC (Chiral MD): $t_R = 15.8$ (major), 20.6 (minor)

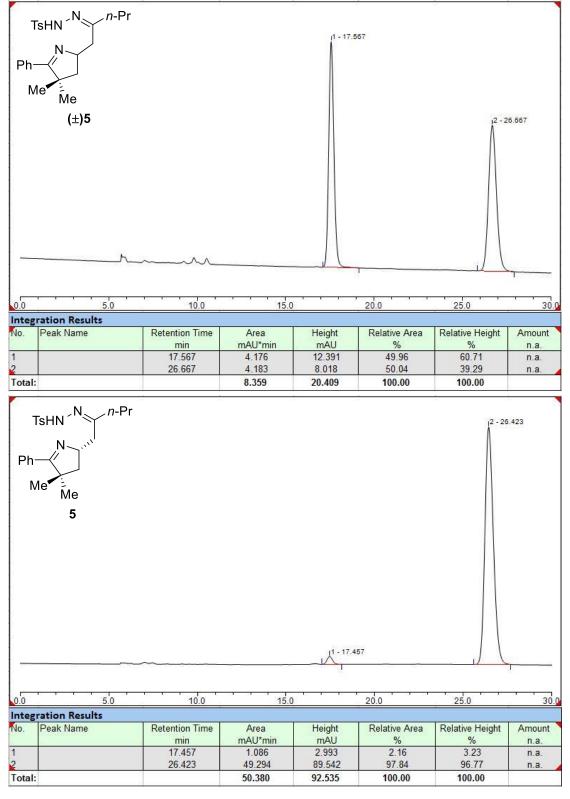


HPLC (Chiralpak AD-H): $t_R = 18.3$ (major), 21.8 (minor)

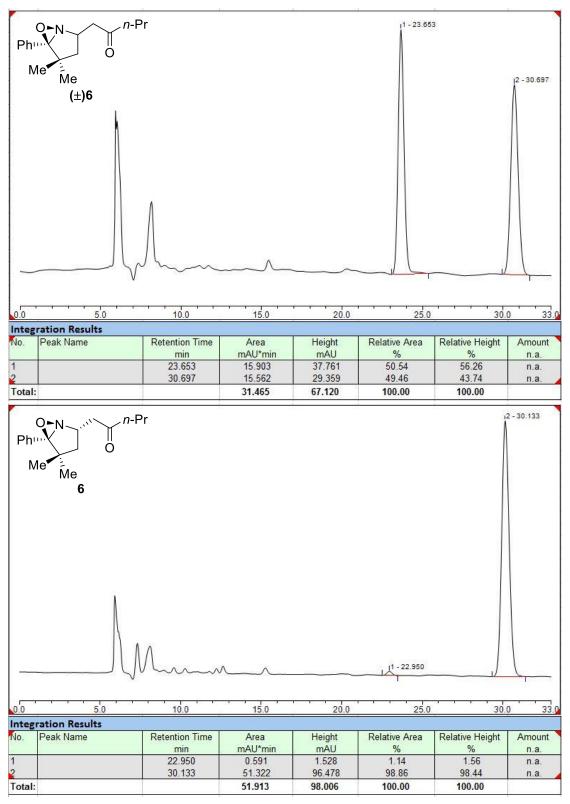


HPLC (Chiralpak AD-H): $t_R = 8.0$ (major), 9.5 (minor)

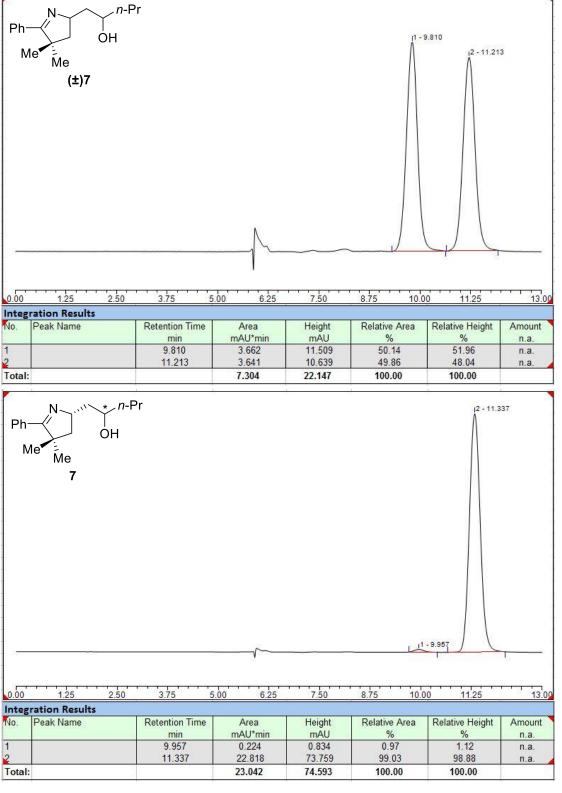
n-Pr



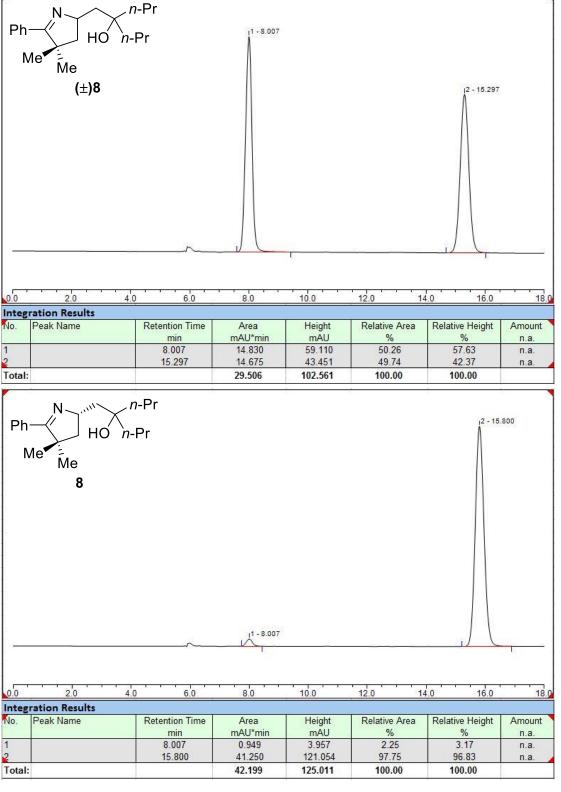
HPLC (Chiral MD): $t_R = 17.5$ (minor), 26.4 (major)



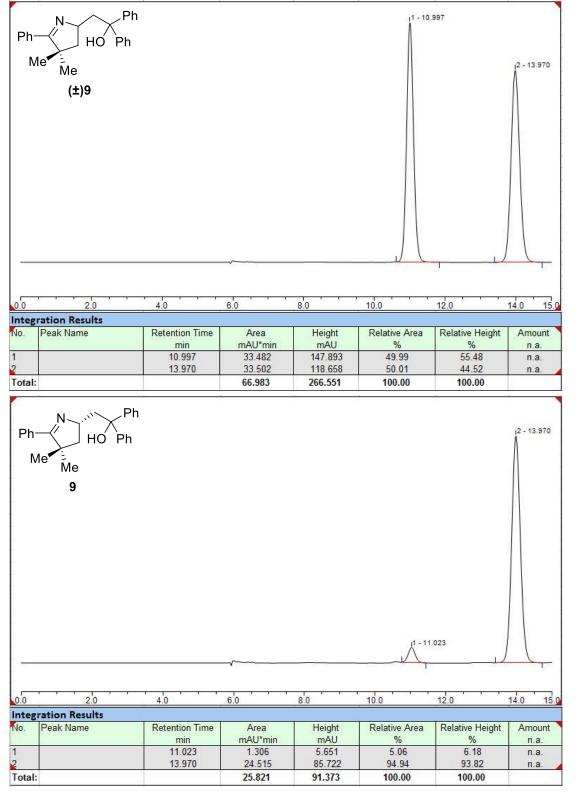
HPLC (Chiral MD): $t_R = 23.0$ (minor), 30.1 (major)



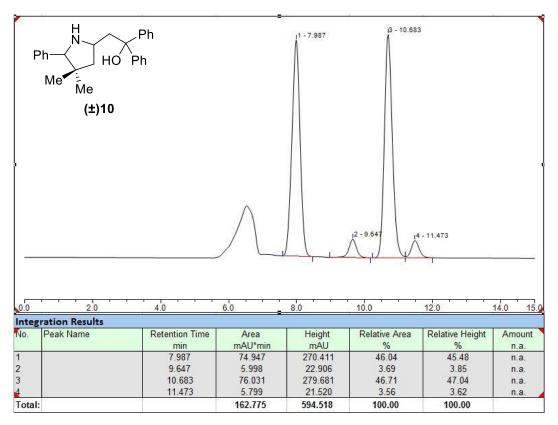
HPLC (Chiral MD): $t_R = 10.0$ (minor), 11.3 (major)

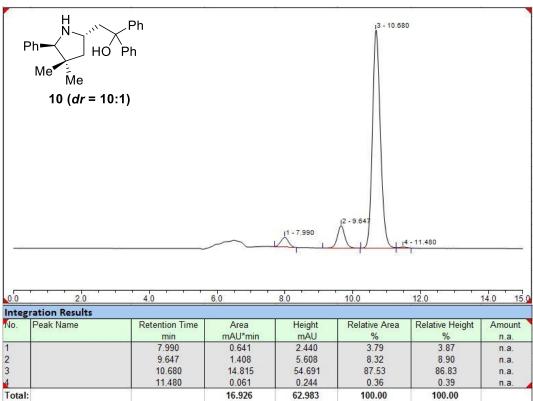


HPLC (Chiral MD): $t_R = 8.0$ (minor), 15.8 (major)

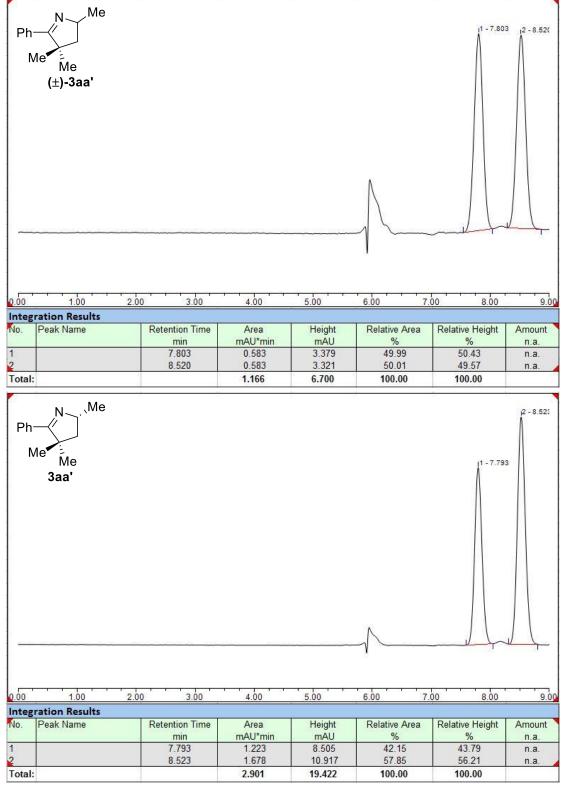


HPLC (Chiral MD): $t_R = 11.0$ (minor), 14.0 (major)





HPLC (Chiralpak AD-H): $t_R = 8.0$ (minor, major diastereomer), 9.6 (major, minor diastereomer), 10.7 (major, major diastereomer), 11.5 (minor, minor diastereomer)



HPLC (Chiral MD): $t_R = 7.8$ (minor), 8.5 (major)